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Studies of the Characteristics of Carbon Formed on Iron and on Nickel Surfaces during Hydrocarbon Synthesis

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Abstract

The kinetics of the hydrogenation of carbon monoxide have been studied using thin films of iron and of nickel on quartz plates. The reactivity of the films was tested for various treatments of reduction and oxidation followed by reduction. The latter treatment reduced considerably the reactivity of both iron and nickel films. The carbon deposited as an intermediate in the reaction was analyzed by SEM and its reactivity towards hydrogen was determined. These characteristics were compared with those of carbon formed by decomposition of carbon monoxide in the absence of hydrogen. Examination by SEM showed no structure or other characteristics of deposited carbon on the films of either iron or nickel. The carbon formed during the reaction was somewhat more reactive towards hydrogen than the carbon formed by decomposition of carbon monoxide. The reaction of H_2 + CO gave minor amounts of unsaturated hydrocarbons, but hydrogenation of the deposited carbon gave only saturated hydrocarbons.

Objectives

A vast literature exists on studies of the methanation of carbon monoxide using various metals as catalysts. In recent years emphasis has been directed towards an analysis of the surface of the catalyst and its relation to the mechanism of the reaction. Of particular interest is the role of carbon as an intermediate in the hydrogenation steps. The present study was directed toward an examination of the characteristics of the carbon formed as an intermediate in the hydrogenation of carbon monoxide using Scanning Electron Microscopy in conjunction with kinetic studies. For this purpose the catalysts iron and nickel were chosen so that by comparing the role of carbon as an intermediate some understanding of the differences in the mechanism of hydrogenation on these metals would be achieved.

Introduction

Carbon has long been recognized as an important intermediate in the hydrogenation of carbon monoxide. It is generally believed to form by dissociative adsorption of carbon monoxide on the metal, but the subsequent steps whereby carbon either accumulates or reacts, are not well understood. By itself, carbon monoxide undergoes disproportionation on metal surfaces to give carbon and carbon dioxide

$$2CO \rightarrow C + CO_2$$

at temperatures in the neighbourhood of 300°C and at moderate pressures. Under these conditions interstitial carbides are formed and eventually cause disintegration of the metal particles (1). Other forms of carbon, described for example, as amorphous, graphitic and filamentous have been observed (2). In the presence of hydrogen, water and hydrocarbons are also formed, but the characteristics of the carbon formed in these systems are highly variable.

Several forms with different reactivity have been reported. It appears that the carbon is most reactive in the initial stages of its formation and may become less reactive as it accumulates or as it is exposed to higher temperatures. McCarty and co-workers (3,4) demonstrated that different states of active carbon formed on supported nickel catalysts by decomposition of carbon monoxide. The reactivity was measured by temperature-programmed surface reaction (TPSR) with hydrogen. At least two types of surface carbon (α and β) were formed by decomposition of carbon monoxide at 525-600 K. It was suggested that the most active type, α, was a dispersed form of atomic carbon which served as intermediate for the formation of methane as well as for the formation of the less active type, β, alternatively referred to as amorphous carbon or polymeric carbon. The conversion of α carbon to the less active β carbon occurs rapidly above 550 K and β carbon converts to an inactive form, graphitic, above 625 K. If the carbon is formed in the presence of hydrogen these intermediate types may be different. Gupta, Kamplo and Iyer (5) showed that in the interaction of methane with supported Ruthenium the yield of hydrogen-deficient carbon (C_2) and monocarbon species (C_1) formed at the catalyst surface depended on temperature and support material, for example, molecular sieve, alumina or glass beads. They also reported that while the hydrogen reacted with these species to give ethane and methane, in its absence the C_2 species transformed with time to the C_1 form, and both converted on standing to a form that was unreactive to hydrogen.

Many studies have been made, using various surface analytical techniques, of the characteristics of the catalyst surface at various stages of the reaction. The adsorption of carbon monoxide on iron and nickel has been extensively studied using infra-red spectroscopy. Some differences in the type of chemisorption have been suggested but dissociation is probably important on both metals. Mossbauer

spectroscopy (6) showed that an iron catalyst (10% Fe on Al_2O_3) exposed to mixtures of CO + H_2 or CO + He at about 550 K formed carbides of various stoichiometries. Auger spectroscopy (7) indicated that when an iron catalyst was treated with synthesis gas (H_2/CO = 3) at 573 K and 6 bar pressure, the surface was rapidly covered by carbonaecous material. It was claimed that the deposit poisoned the catalyst, since a slow increase in carbon deposition caused a slow decrease in catalytic activity. This carbon, however, differed from the carbidic carbon in being completely dehydrogenated, crystalline and graphitic. Measurements by scanning electron microscopy following decomposition of carbon monoxide on reduced iron oxides (773 - 830 K) confirmed the existence of carbides, as rectangular transparent particles, and carbon, as hollow filaments (8). The carbidic carbon probably includes C_{ads}, CH_{ads}, CH_{2ads}, CH_{3ads} and other polymeric species.

A TPSR study of the methanation reaction of carbon monoxide (9) using Ni, Ni-Y, Ni-La, and Ni-K supported on α-Al_2O_3, revealed two types of intermediate carbonaceous species. Only one reacted to form hydrocarbons. Detailed XPS and AES line-shape analysis suggested that during the reaction the adsorbing layer consisted of a family of surface species ranging from amorphous carbon to mono or polymeric species (10). Dalmon and Martin (11, 12) suggested that in the hydrogenation of carbon monoxide over nickel catalysts the active species is the carbide, Ni_3C, formed on the surface.

It appears that the characteristics of the carbon and the carbidic species may be quite different for the two metals, iron and nickel. The present experiments were designed to examine, using Scanning Electron Microscopy (SEM) the carbon deposit formed at various stages of the hydrogenation of carbon monoxide on both iron and nickel catalysts. For this purpose the catalyst was prepared as a thin film on quartz plates which were removed from the reactor for the SEM analysis. The carbon was examined following decompo-

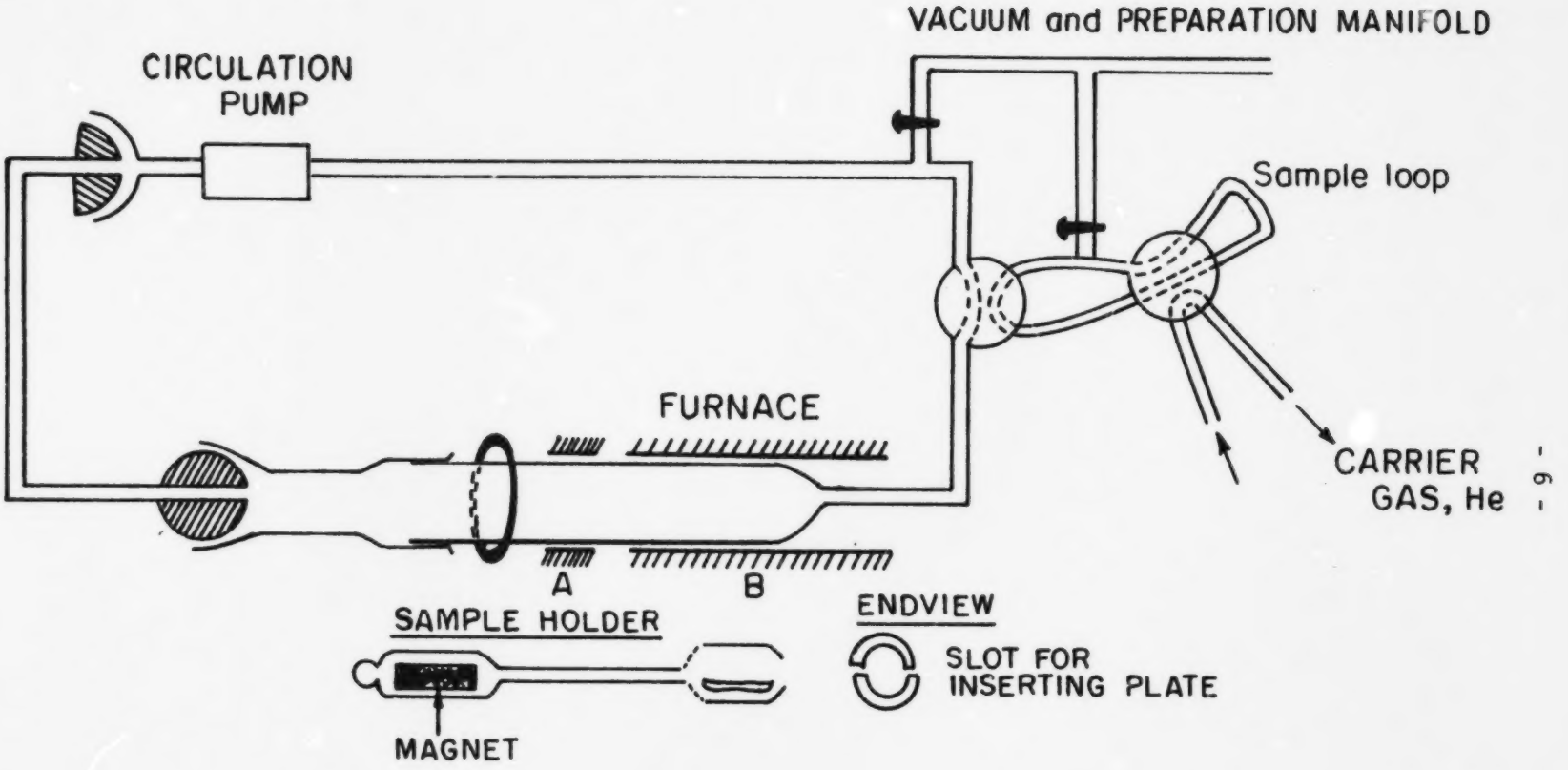
sition of carbon monoxide and following reaction of carbon monoxide and hydrogen. The reactivity of the carbon with hydrogen was also measured and the effect of this reaction on the surface carbon was also examined by SEM.

Experimental

(a) Apparatus

A schematic diagram of the apparatus is given in Figure 1. The reaction vessel was part of a circulation system. The catalyst was prepared on quartz plates, 1 mm thick (described later), which were accommodated in a sample holder. The holder could be removed from the furnace using a magnet without admitting air to the reactor. In each experiment two large quartz plates, 7.1 x 1.1 cm^2 and four small plates, 0.2 x 0.5 cm^2 (for SEM analysis), were used. The plates were supported so that the metal surfaces were well exposed to the reactants. The auxiliary furnace A was used for oxidation and reduction of the catalyst prior to reaction and the furnace B was used for the main reaction. Reactants were admitted to the desired pressure and mixed by the circulation pump while the catalyst was outside the furnace. Mixing was complete within five minutes. The reaction was started by moving the sample holder into the furnace using the magnet. Samples were withdrawn for analysis through a 4-way stopcock and 6-port valve. The total volume of the reactor was about 300 mL, the volume of the sample loop was 1 mL and the total volume of the sampling arrangement was about 2 mL.

Products were analyzed using a carbosieve G column, 4' x 1/8", at 180°C. Hydrocarbons were analyzed using a Hewlett Packard Gas Chromatograph Model 5706A with FID detector. Carbon monoxide was analyzed by the same column but using a thermal conductivity detector. Hydrocarbons and carbon dioxide were calibrated in the presence and absence of carbon monoxide and hydrogen, but no appreciable effect of the diluent was observed. Calibration factors for methane, ethane, ethylene, propane and carbon dioxide in the absence of carbon monoxide or hydrogen are given in the Appendix.



1. Schematic diagram of the apparatus.

(b) Preparation of Catalysts

(i) The Edwards Sputter Coater, Model S150A was used to prepare metal films on quartz plates. Two cathodes were made, one of mild steel for the iron films and one of copper plated with nickel for the nickel films. Nickel was electroplated on the copper cathode by Zenith Co. Ottawa. The total amount of iron on a quartz plate was quantitatively analyzed by the use of Direct Current Plasma Spectroscopy. The film of iron was dissolved in 5 mL of hydrochloric acid and diluted to 100 mL with distilled water. Nickel films were dissolved in 5 mL of aqua-regia and evaporated to dryness. The residue was dissolved in 5 mL of hydrochloric acid and diluted to 100 mL with distilled water.

The quartz plates were boiled in aqua regia, rinsed thoroughly with distilled water and then cleaned ultrasonically in chloroform.

Each metal was sputtered on two plates of similar area simultaneously and the amount of metal on each plate was the same within 5%. This suggests that a fairly uniform film was obtained for both metals. The optical density of the plates provided a convenient method of determining the concentration of metal in the film. Calibration was made by dissolving the metal as described, and a calibration curve for iron is shown in the Appendix. The optical density as a function of wave length for iron and nickel is also given in the Appendix.

(ii) Films of iron and nickel were also prepared from solutions of the respective ions. A small drop, 0.1 L of solution, 0.01 M, was dried and heated to 400°C followed by reduction with hydrogen. These films were used only for decomposition of carbon monoxide.

(c) Materials

Carbon monoxide (99.99%) was obtained from Air Products. Other hydrocarbons and hydrogen were obtained from Matheson Co. The ferrous and nickel nitrate were Fisher Reagent Grade.

Summary of treatments for metal films

The following describes the various treatments given to the metal films before particular reactions.

A. Untreated: used as obtained from the Sputter Coater.

B. Oxidation and Reduction Treatment

Oxidation	followed by	Reduction
Pressure of air: 1 atm		Pressure of H_2: 500 Torr
Time of oxidation: ½ hour		Time of reduction: 2 hours
Temperature, K		Temperature, K
1. 1083		774
2. 1083		1083
3. 973		1073
4. 673		773

C. Reduction of untreated films

Pressure of H_2: 400 Torr

Temperature: 573 K

Time of reduction: 2 hours

Results

The results are presented in Tables and in Figures. The figures show the yields of products as a function of time, which show the importance of the induction period in the reactions with the iron films. The tables summarize the rates of formation of methane (maximum rates for experiments with induction periods) and the selectivities of methane for the various reaction conditions. Selectivity is calculated as

$$S = \frac{\text{Pressure of } CH_4}{\Sigma \text{ (Pressure of all hydrocarbon products)}}$$

The tables also summarize the final yields of products and the recovery of carbon from the film. The final tables at the end summarize all the results.

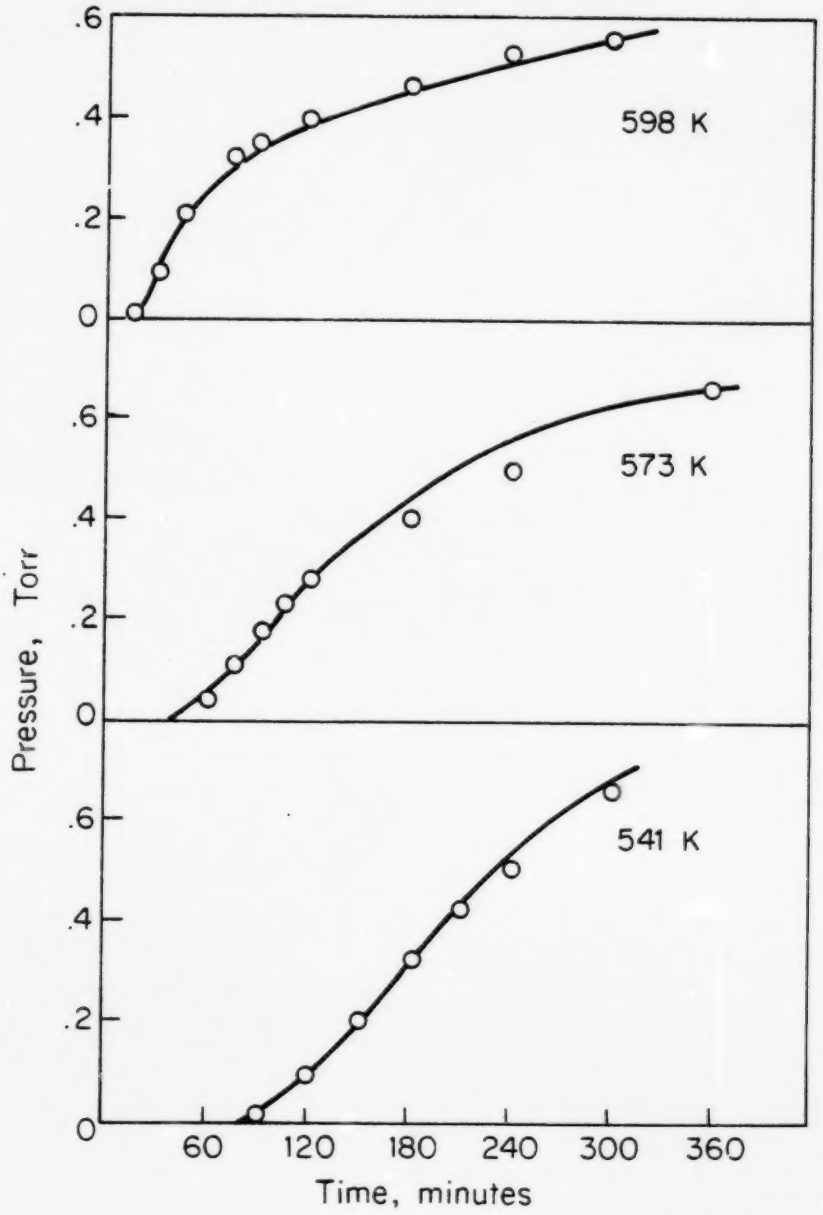
Kinetic Studies of the CO + H_2 reaction

A. Untreated iron films

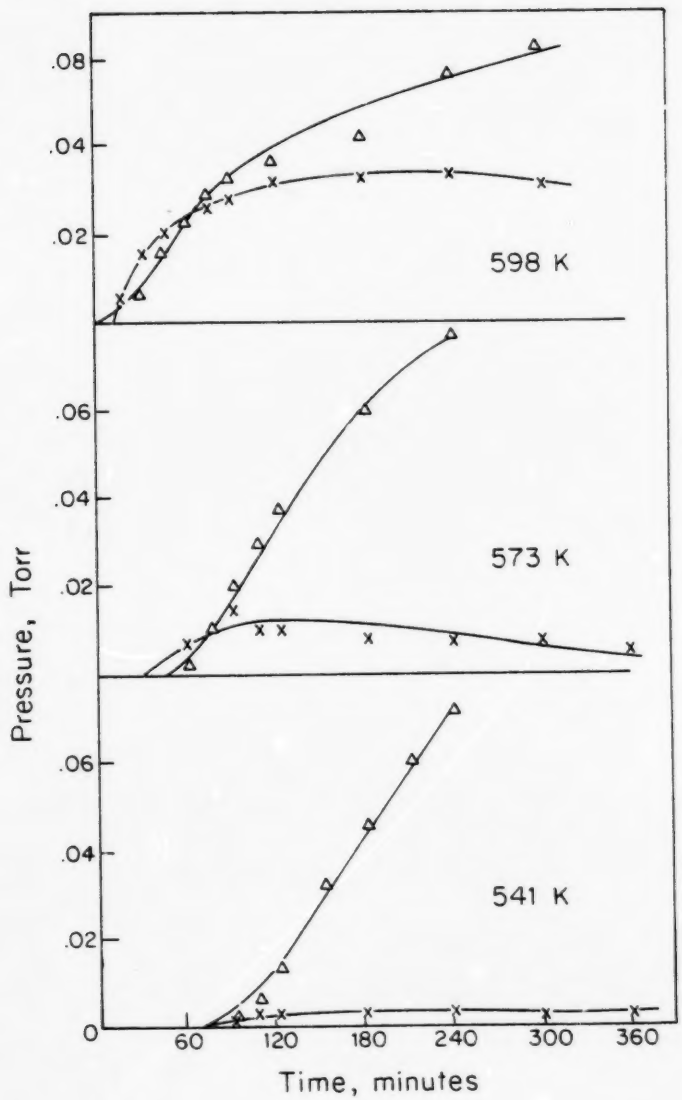
(a) The first experiments were done using iron films with a total weight of 280 μg per plate. Using a density of iron of 7.86 g mL^{-1} the thickness of the films was approximately 23 nm (assuming uniformity). The yields of products as a function of time were measured at three temperatures, 541, 573 and 598 K using a ratio of H_2/CO of 55 and a total pressure of 480 Torr. At 523 K the reaction was too slow to measure conveniently, with an induction period of about six hours and only 0.008 Torr of methane produced after 405 minutes. Methane was the main product with small amounts of ethane and ethylene. The measurements are shown in Figures 2 and 3. The induction period decreased with increasing temperature. At longer times the yield of ethylene decreased and after 24 hours the yields of ethylene and ethane were comparable.

(b) Effect of the intermediate carbon on the reaction

The effect of carbon formation during the induction period was tested in the following way. A series of reactions was performed at 573 K under conditions



2. Yield of methane as a function of time at temperatures 541, 573 and 598 K.



3. Yields of products ethane and ethylene as a function of time at three temperatures, 541, 573 and 598 K.
△ : ethane; x : ethylene

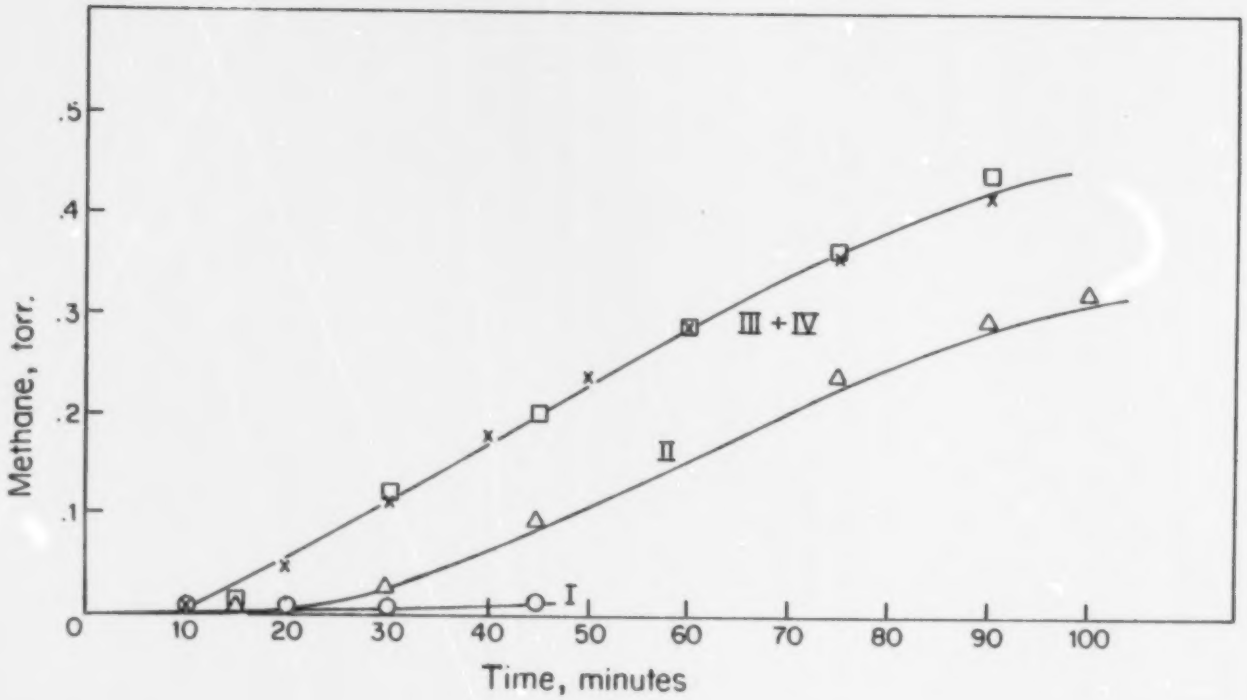
similar to those described in (a). The first reaction, I, was allowed to proceed for 40 minutes, about the end of the induction period (Figure 2). The reactant and products were removed and reaction II was started by introducing fresh reactants. The curve, designated II in Figure 4, was obtained, showing that the induction period was shortened. This reaction was allowed to proceed for 110 minutes while products accumulated and the reactants and products were again removed. Reaction III was started by admitting fresh reactants. The induction period was again shortened. On continuing the same process, reaction IV appeared to show no appreciable change from reaction III (Figures 4 and 5). The maximum rate for methane formation was almost constant for all reactions. From these results it may be concluded that carbon, or other species formed during the induction period which was not removed by evacuation, was an intermediate in the reaction. This intermediate species was essential for the formation of methane. The maximum rate of methane formation was almost constant for all the reactions, which indicates that no poisoning effect of the intermediate occurred on the surface.

(c) Effect of weight of iron in the film

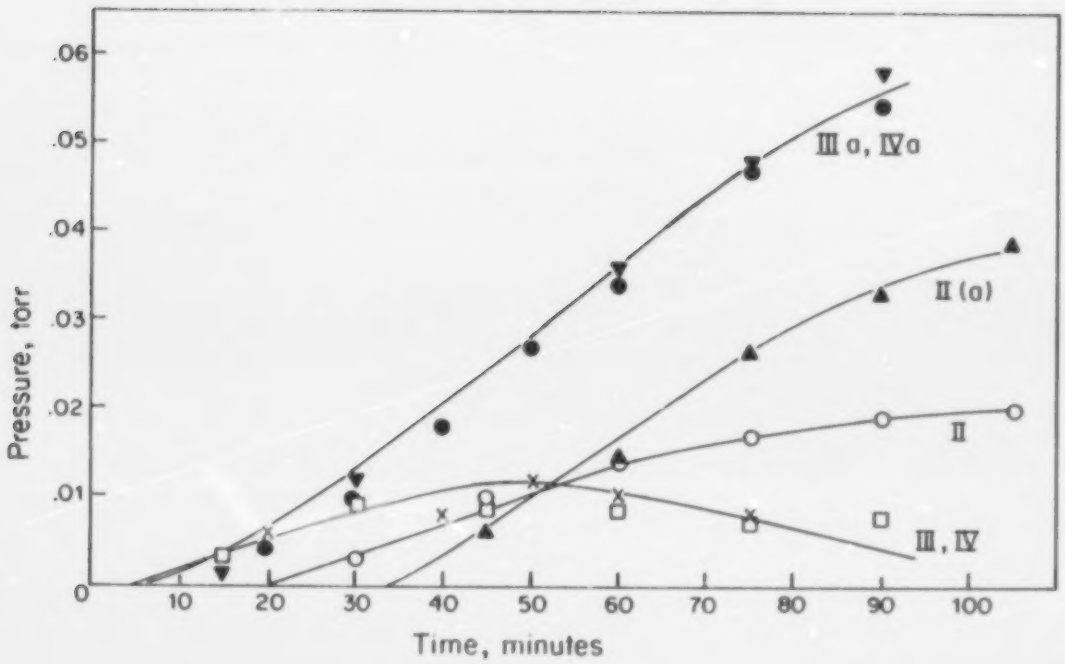
Films of iron were made with 480 μg per plate. Yields of products as a function of time with conditions the same as (a) are shown in Figure 6. The main change was in the product distribution. The yield of ethylene was greater than that of ethane in the early stages, but at longer times the yield of ethylene decreased and after 24 hours the yields were comparable. Subsequent experiments were done using films with about 480 μg per plate.

(d) Effect of H_2/CO ratio

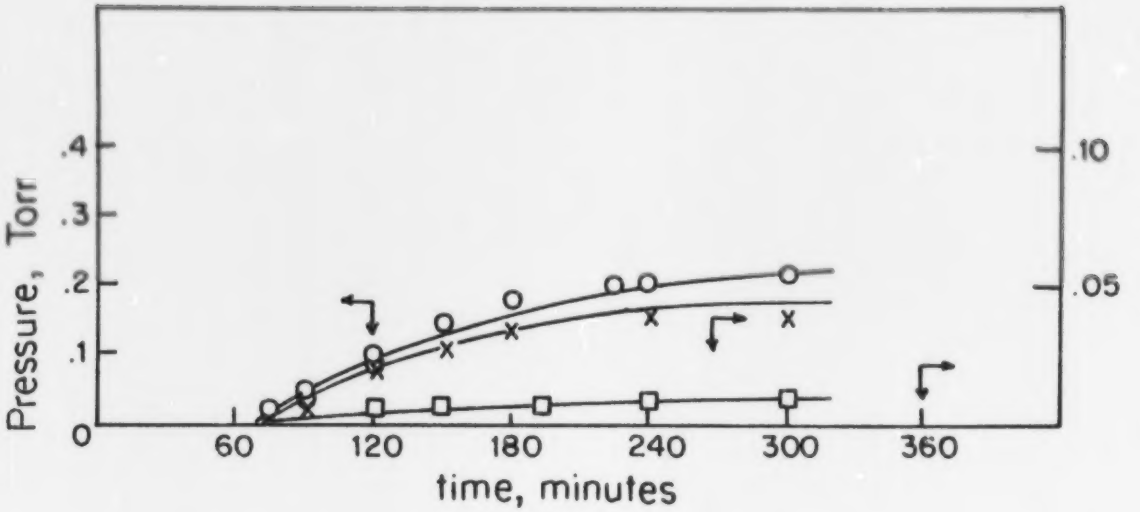
Rates were measured for ratios of H_2/CO of 2, 5 and 55 at 573 K, at a total pressure of 480 Torr. The yields of products for these reactions are given in Figures 7, 8, 9 and 10. The induction period decreased with increasing ratio of



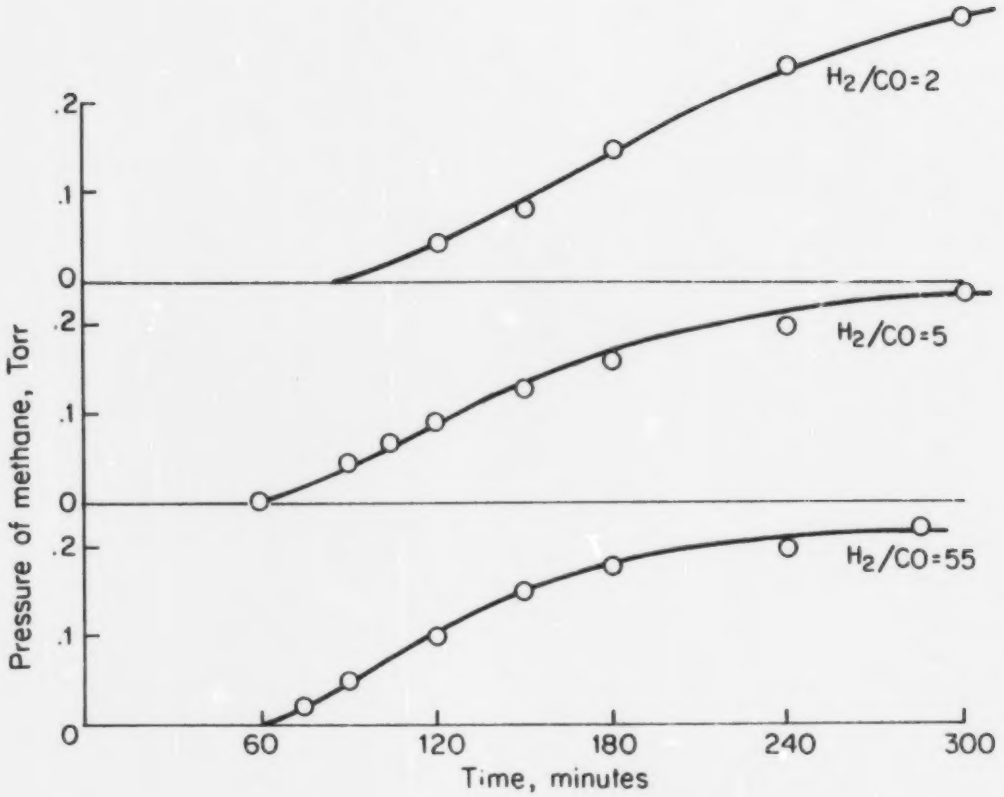
4. Yield of methane for a series of reactions in which products and reactants were removed after successive reactions. T = 573 K; Total pressure : 480 Torr; $\frac{H_2}{CO}$ = 55.
○ : first reaction ; △ : second reaction
□ : third reaction ; x : fourth reaction



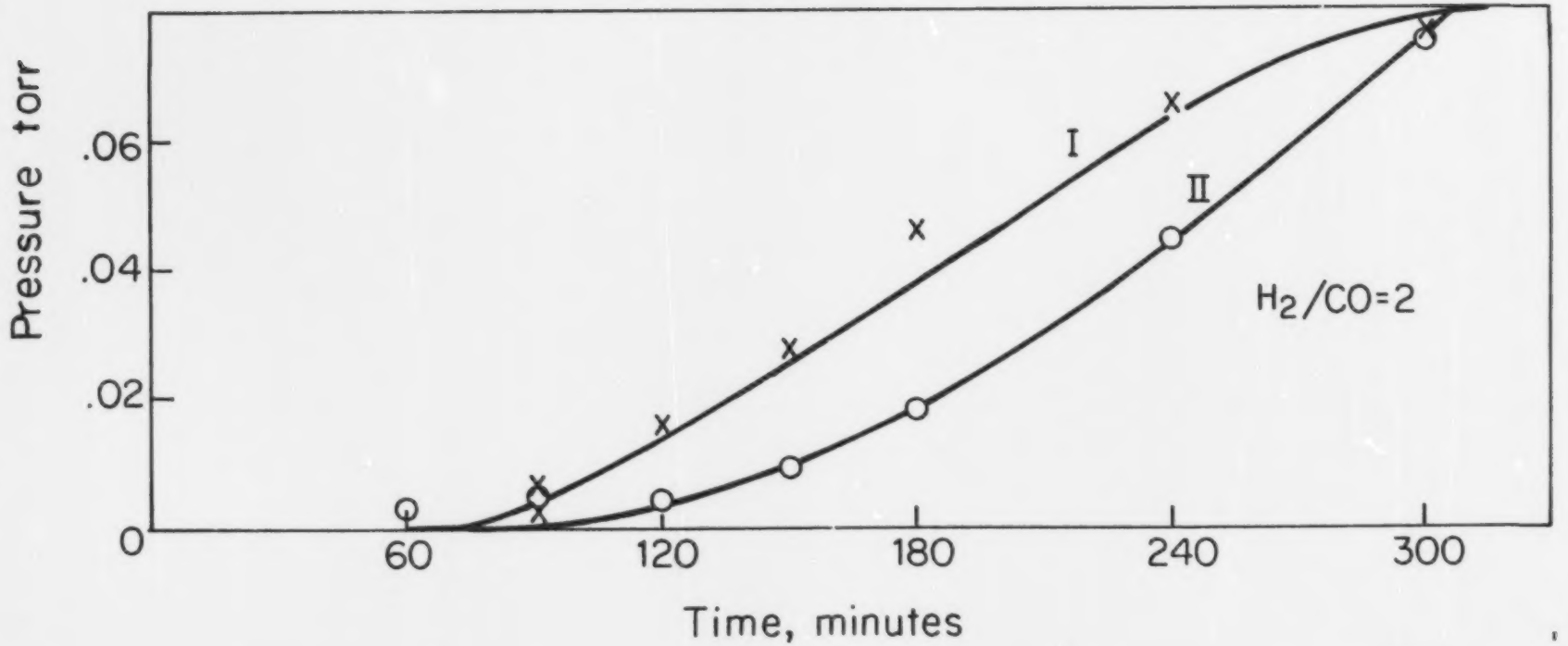
5. Yields of ethane and ethylene for a series of reactions in which products and reactants were removed after successive reactions.
T = 573 K; Total pressure : 480 Torr; $\frac{H_2}{CO}$ = 55.
Ethane: ▲ : second reaction
▼ : third reaction
● : fourth reaction
Ethylene: ○ : second reaction
□ : third reaction
x : fourth reaction



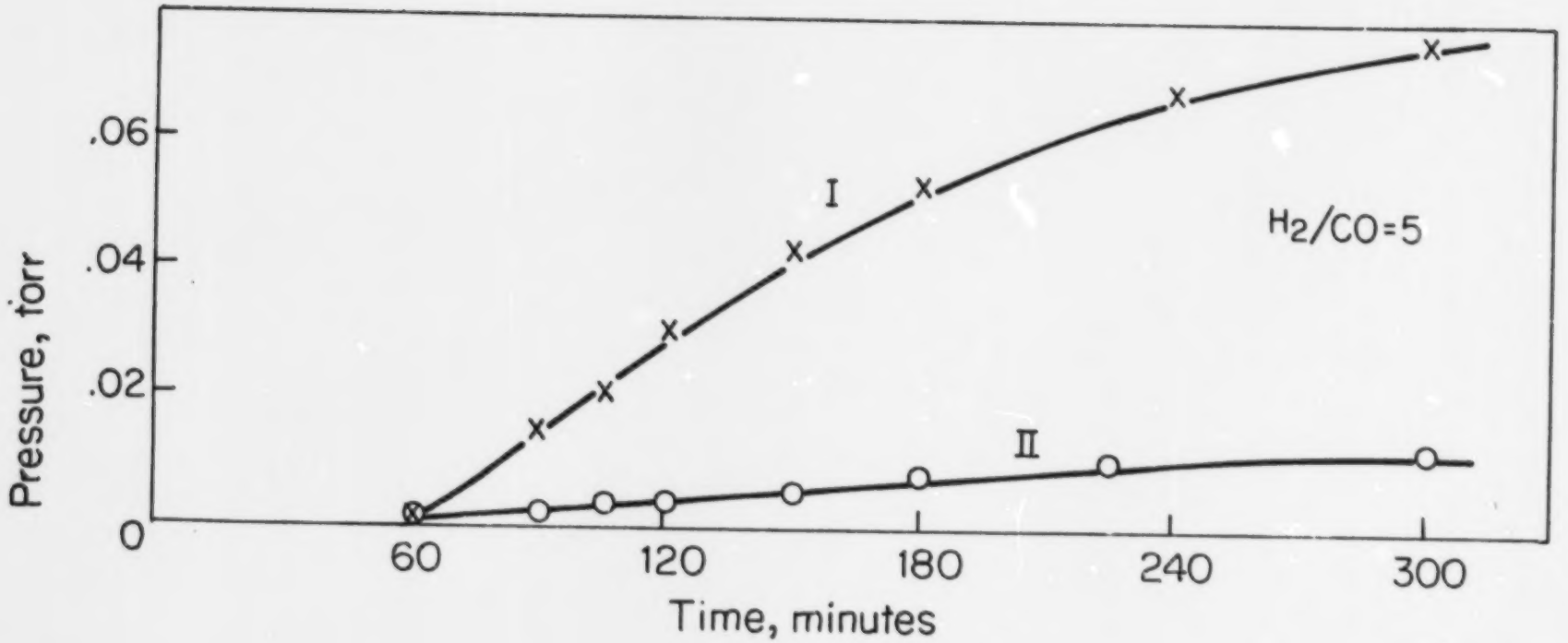
6. Yields of products as a function of time.
Total pressure: 480 Torr; $\frac{H_2}{CO}$ = 55; T = 573 K
Total Fe = 480 μg per plate.
○ : methane; x : ethylene; □: ethane



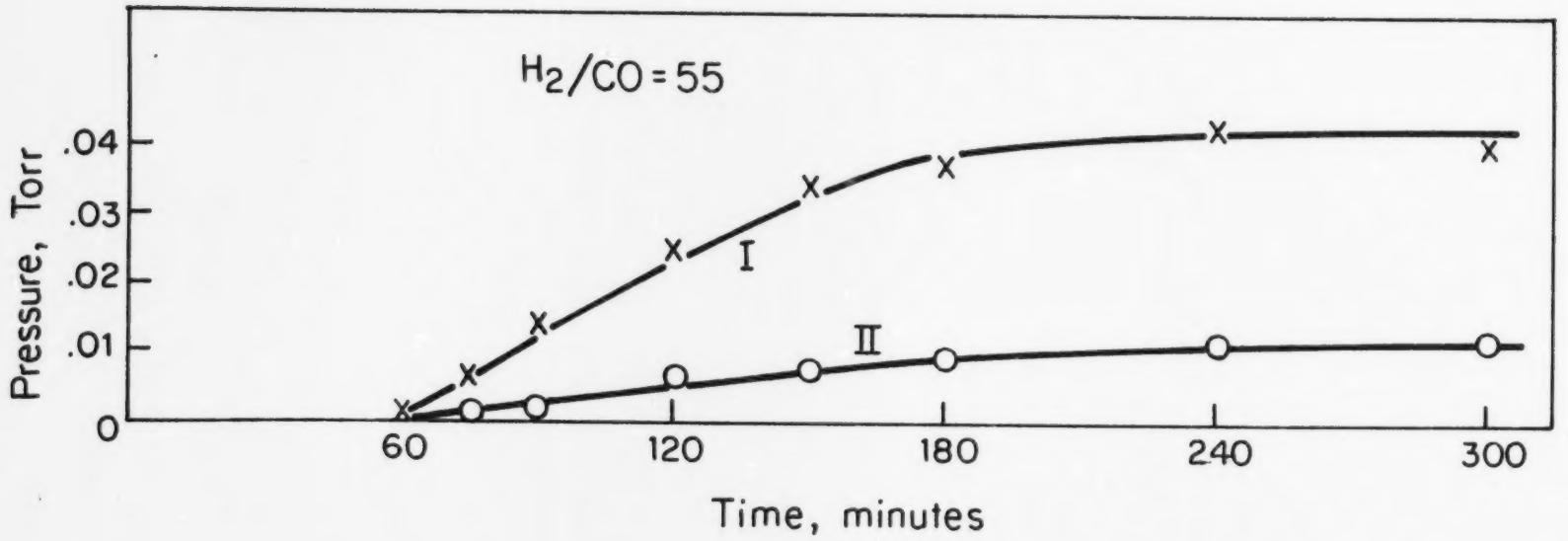
7. Yield of methane as a function of time for various ratios of H_2/CO. T = 573 K. Total pressure = 480 Torr.



8. Yield of products as a function of time
Total pressure 480 Torr; T = 573 K
O: ethane; x : ethylene



9. Yield of products as a function of time
Total pressure 480 Torr; T = 573 K
O: ethane ; x : ethylene.



10. Yield of products as a function of time.
Total pressure 480 Torr; T = 573 K
○: ethane ; x : ethylene

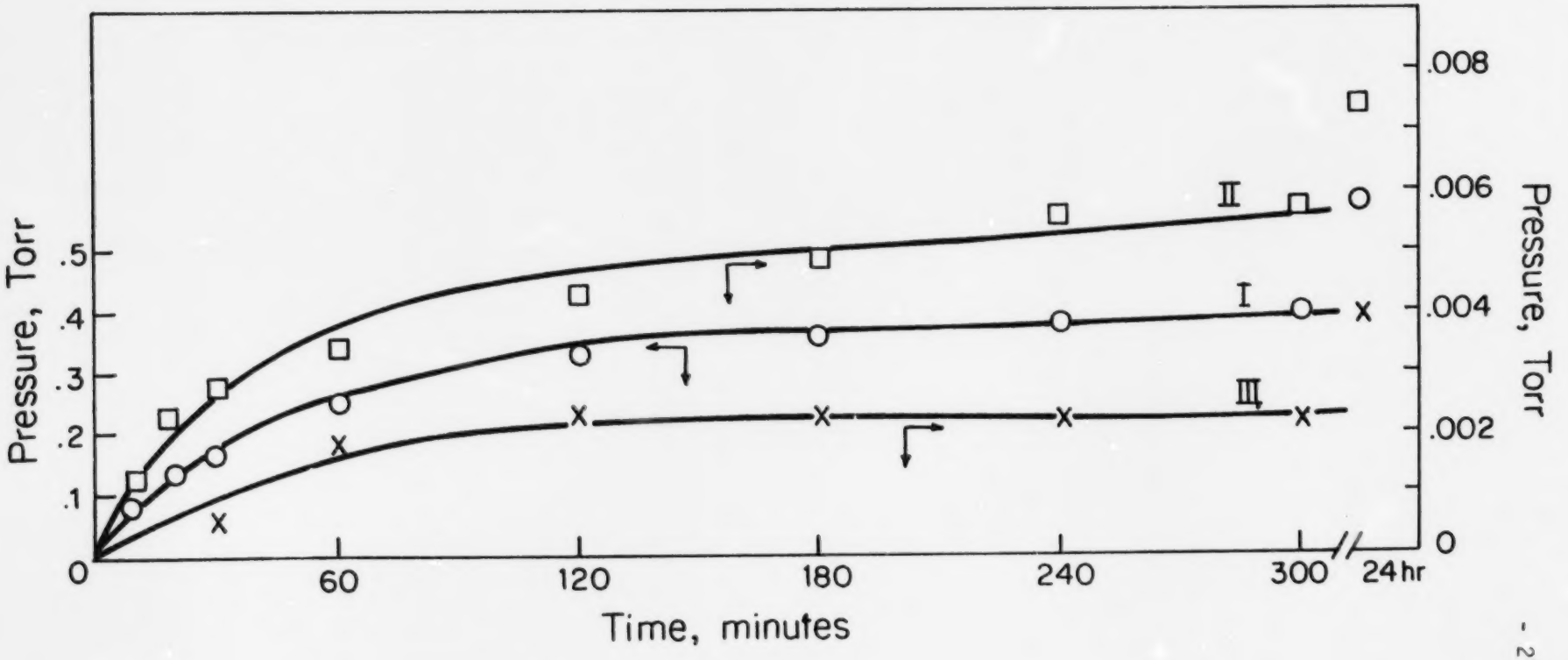
H_2/CO but the rate of formation of methane was practically unchanged. The change in ratio had more effect on the relative yields of ethane and ethylene. At the lowest ratio the yields were close but as the ratio was increased the yield of ethylene became more pronounced. At the highest ratio the yield of ethylene had decreased slightly, which is probably the result of secondary reactions.

(e) Hydrogenation of deposited carbon

The carbon deposited on the surface during the reaction of H_2 + CO was hydrogenated at 673 K with 450 Torr of hydrogen. The surface was first flushed with helium to remove adsorbed carbon monoxide. Methane was the main product with small amounts of ethane and propane. Ethylene was detected in the early stages of the reaction and then disappeared, probably due to further hydrogenation. Yields as a function of time are given in Figure 11 and the selectivities of the products are given in Table 1.

The kinetics of the formation of methane by the hydrogenation of carbon on the surface may be compared with the kinetics of its formation from the reaction of H_2 + CO. No induction period was observed in the formation of methane from reaction of hydrogen with the surface carbon and the selectivity for methane was slightly greater (0.98). The rate of formation of methane was not greatly different. It should be remembered, however, that the temperature in the hydrogenation of surface carbon, 673 K, was higher than in the reaction, 598 K.

To test for complete removal of carbon by hydrogenation, the iron film was oxidized at 798 K in the presence of 500 Torr of air. The carbon dioxide formed by this oxidation was analyzed as a function of time until complete oxidation had occurred. From the final yield of carbon dioxide it was concluded that about 60% of the carbon formed during the reaction of H_2 + CO reacted with hydrogen to form hydrocarbons.



11. Yields of products as a function of time from the hydrogenation of carbon. Pressure of H_2 = 450 Torr. T = 673 K.
○ : methane; □ : ethane; x : propane

Table 1

Selectivities of Products

A. Reaction of H_2 + CO

Temperature, K	Weight of Fe	$\frac{H_2}{CO}$	Selectivity CH_4
573	280 µg	55	0.85
	480 µg	55	0.78
	480 µg	2	0.69

B. Hydrogenation of Carbon deposited during reaction

Pressure of H_2 : 400 Torr

		CH_4	C_2H_6	C_3H_8
673	480 µg	0.98	0.014	0.006

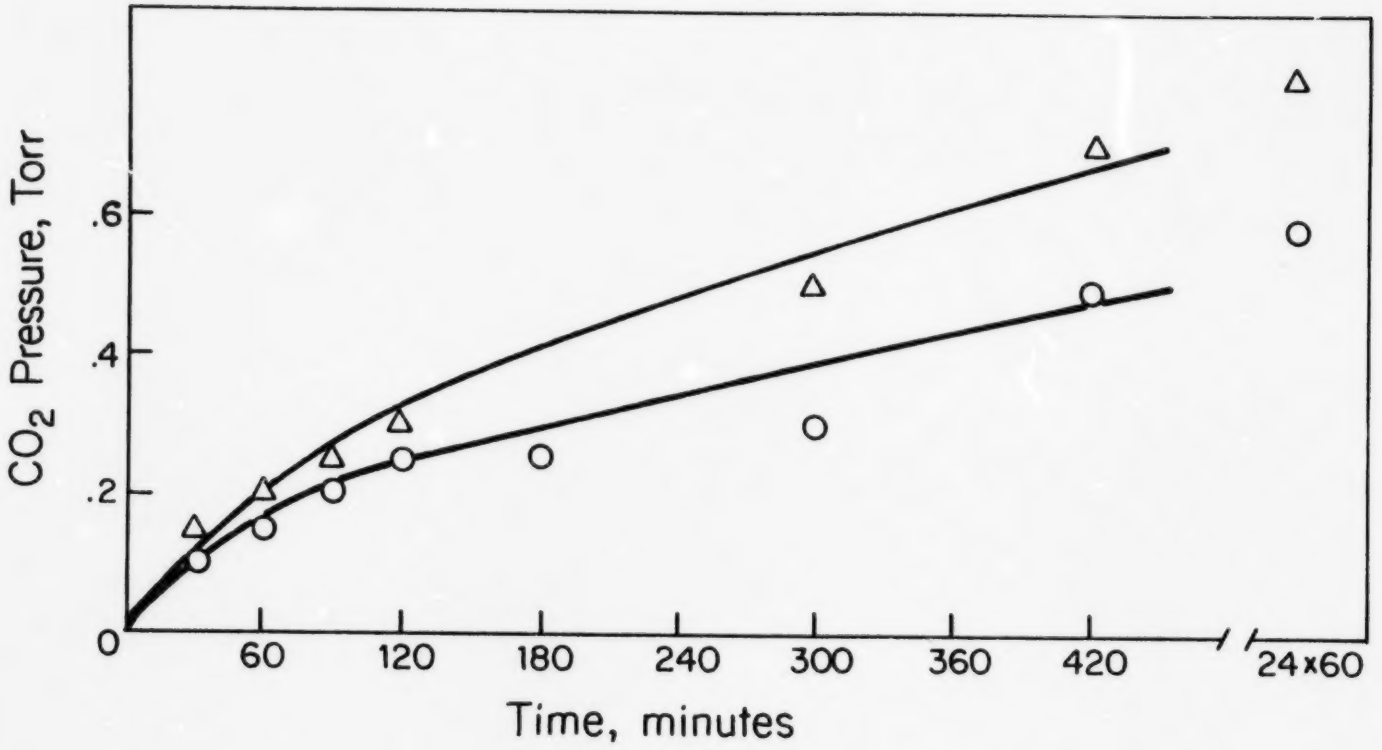
(f) Decomposition of carbon monoxide on iron films.

Carbon monoxide was decomposed over iron films at 573 K with pressures of CO of 82 and 450 Torr. To keep the total pressure constant 368 Torr of helium was added to 82 Torr of CO. The yield of CO_2 as a function of time is shown in Figure 12. The final yield of CO_2 after 24 hours reaction time was 0.75 from 450 Torr of CO and 0.50 Torr from 82 Torr of CO.

The carbon deposited on the surface from the reaction of 82 Torr of CO was hydrogenated at 673 K with 450 Torr of hydrogen. The main product was methane with about 1% ethane. After 360 minutes of reaction time, the gaseous mixture was evacuated and fresh hydrogen was introduced and the methanation was continued for another 24 hours. A third reaction was also made and a small amount of methane was collected. The total methane obtained was 0.45 Torr and ethane was 0.008 Torr. Thus the total carbon recovered by reaction with hydrogen was about 90%, which is within the error of measurement.

B. Oxidized and Reduced Iron Films

(a) Using conditions similar to those described in A(a) a barely measurable reaction was obtained with the oxidized and reduced films. Four sets of oxidation and reduction treatments were tried with temperatures of oxidation between 673 and 1083 K and temperatures for reduction the same or higher. In each case only traces of products were obtained. Using an iron film oxidized at 973 K and reduced at 1073 K a reaction was allowed to proceed for 450 minutes. Products and reactants were removed and fresh hydrogen was introduced at 673 K to test for the presence of carbon on the surface. Only 0.0015 Torr of methane was formed. Reasons for this reduced activity of the oxidized and reduced films will be discussed later.



12. Yield of CO_2 from the decomposition of carbon monoxide over iron films. T = 573 K.
○: pressure of CO = 82 Torr; pressure of He = 380 Torr
△: pressure of CO = 450 Torr

(b) Decomposition of Carbon Monoxide

Conditions similar to those of A(f) were used for the decomposition of carbon monoxide on iron films oxidized at 673 K and reduced at 773 K (B.4). The rate of decomposition of carbon monoxide over these films was much slower than over the untreated films. The final yield of carbon dioxide was barely measurable (0.07 Torr after 24 hours). The deposited carbon was hydrogenated after removing the gaseous mixture as described in A(f). Two consecutive hydrogenations were made. From the total hydrocarbons formed in both reactions, 0.031 mole of carbon reacted. Therefore less than 50% of the deposited carbon was recovered by hydrogenation. Thus the carbon formed on the untreated film was definitely more active for hydrogenation than the carbon formed on the surface of the oxidized and reduced iron.

C. Iron Films Reduced in Hydrogen

Since the iron films prepared by sputtering would be expected to contain some oxide, some experiments were done to test the effect on the reaction of reducing the films with hydrogen before the reaction (Treatment C). The reaction was studied using a ratio $H_2/CO = 2$ with a total pressure of about 480 Torr and at a temperature of 573 K. The results are summarized in Table 2.

The iron films were then hydrogenated at 673 K to recover the deposited carbon as described in A(e). The results are given in Table 2 and Figure 13. The rate of methane formation from this reaction is somewhat less than the rate obtained from the methanation of carbon on the untreated iron film. The selectivity for methane formation is, however, approximately the same. On oxidizing the remaining carbon from the surface the total carbon dioxide obtained was 0.37 Torr, indicating that again about 60% of the deposited carbon was hydrogenated. The total carbon deposited on the reduced iron surface was less than on the untreated iron film. These results indicate that reduction of the iron films before reaction makes

Table 2

Iron films reduced in hydrogen before reaction

(a) Reaction with H_2 + CO

Pressure of H_2 = 323 Torr T = 573 K

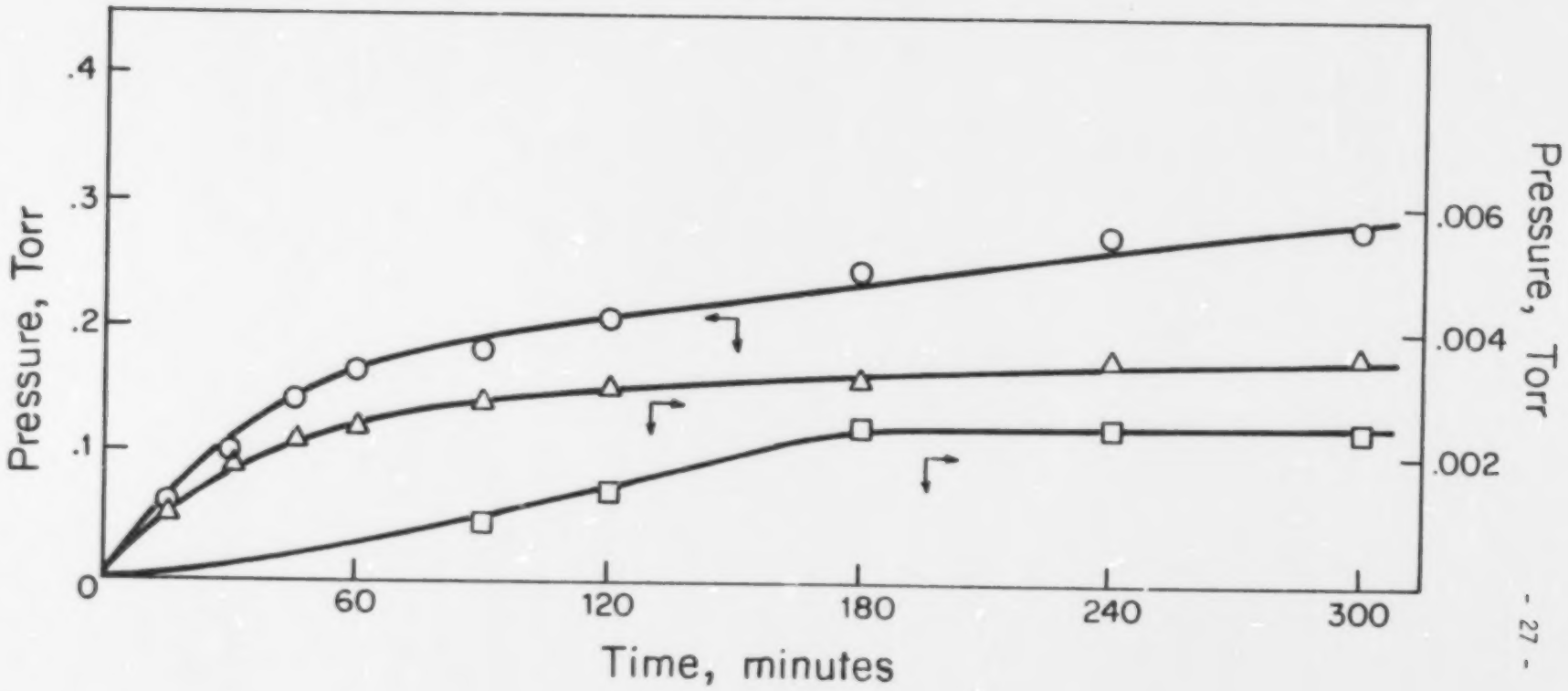
Pressure of CO = 163 Torr

	Yield of Products after 24 hours / Torr	Selectivity for CH_4	Rate of formation of CH_4 / Torr min^{-1}
CH_4	2.40	0.81	3.3×10^{-3}
C_2H_4	0.14		
C_2H_6	0.18		
C_3H_6	0.01		
C_3H_8	0.01		

(b) Hydrogenation of surface carbon

T = 673 K Pressure of H_2 = 400 Torr

	Yield of Products after 24 hours / Torr	Selectivity for CH_4	Rate of formation of CH_4 / Torr min^{-1}
CH_4	0.491	0.98	3.7×10^{-3}
C_2H_6	0.006		
C_3H_8	0.003		



13. Yields of products from the hydrogenation of the iron films following reaction in Part C.
Pressure of H_2 = 450 Torr; T = 673 K
○: methane; △: ethane; □: propane

little difference to the over-all kinetics of the reaction.

D. Oxidized iron films

The untreated iron films, used for the H_2 + CO reaction (A(a)), hydrogenated to remove the active carbon and then oxidized in air to remove all the carbon, were tested for reactivity by repeating the reaction with H_2 + CO mixtures. The initial rate and the selectivity for methane formation are given in Table 3 for comparison with the reactivity on the other iron films. This result shows that the oxide of iron is active for the H_2 + CO reaction. Further studies were not made.

E. Untreated Nickel Films

(a) H_2 + CO reaction

Nickel films were prepared using the Edwards Sputter Coater with the copper cathode electroplated with nickel. No copper was detected in the film by X-Ray analysis. Conditions for the reaction were similar to those used for iron films (A(a)). Methane was the major product with measurable amounts of C_2 and C_3 hydrocarbons. The kinetic characteristics of the reaction over nickel films were different from the reaction over iron films. No induction period was observed and the yields of products usually tended toward a plateau value with time. Figure 14 shows the yield of methane as a function of time. The initial rate of methane formation was 2.1×10^{-3} Torr min^{-1}. The final amount of hydrocarbons obtained in 24 hours reaction time are given in Table 4.

After 24 hours of reaction time, the system was evacuated and the temperature of the furnace was raised to 673 K. The system was flushed with helium (200 Torr). Fresh hydrogen was introduced to recover the deposited carbon. From the hydrogenation, methane was the main product with 2% ethane and 1% propane. The rate of formation of methane was 5.4×10^{-3} Torr min^{-1}. The total carbon recovered was equivalent to 0.65 Torr. The remaining carbon was oxidized at 798 K in air (500 Torr) and

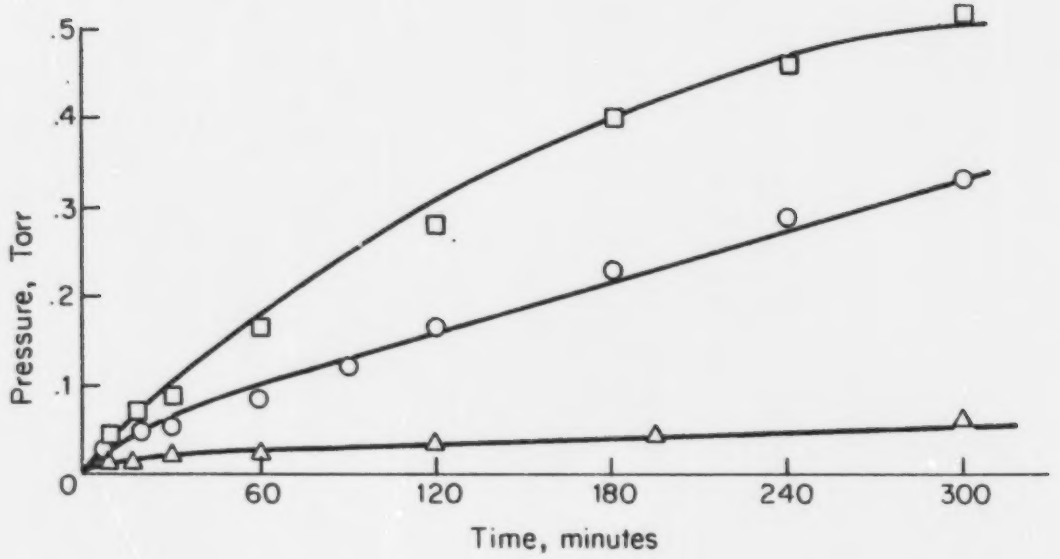
Table 3

Reaction of H_2 + CO using oxidized iron films

T = 573 K Pressure of H_2 = 324 Torr

Pressure of CO = 162

	Yields of Products after 5 hours Torr	Selectivity for CH_4	Rate of formation of CH_4 Torr min^{-1}
CH_4	0.169	0.91	2.2×10^{-3}
C_2H_4	0.014		
C_2H_6	0.010		
C_3H_6	trace		
C_3H_8	trace		



14. Yield of methane from the reaction of H_2 + CO over nickel films. T = 573 K. Pressure of H_2 = 324 Torr; Pressure of CO = 162 Torr.
○: untreated Ni films
□: Ni films treated with H_2
△: oxidized and reduced Ni films

Table 4

Reaction of H_2 + CO over Ni films

Yield of Product after 24 hours. Torr	Treatment of Ni films: Untreated	Reduced	Oxidized + Reduced
CH_4	1.40	2.37	0.290
C_2H_4	.005	.017	.006
C_2H_6	.090	.148	.016
C_3H_6	.003	.007	—
C_3H_8	.017	.023	—
Initial rate of formation of CH_4 Torr min^{-1}	2.1×10^{-3}	4.2×10^{-3}	0.75×10^{-3}

0.22 Torr of CO_2 was obtained. The total carbon dioxide recovered was therefore about 25% of the total carbon recovered. The carbon deposited on this nickel film therefore appears somewhat more reactive than that formed on the iron surface. The optical density of the nickel plate after reaction was higher than the original plate.

F. Nickel Films Reduced in Hydrogen

The H_2 + CO reaction was measured under the same conditions used in E. The results are given in Figure 14 and Table 4. With the reduced film the rate of methane formation (4.2×10^{-3} Torr min^{-1}) was higher than obtained over the untreated nickel film, which is opposite to the trend observed with the iron films treated in a similar way.

The deposited carbon was hydrogenated as before to recover the active carbon. The products were methane, ethane and propane. Virtually no ethylene or propylene were detected. The total carbon hydrogenated ($CH_4 + C_2H_6 + C_3H_8$) was 0.45 Torr. On oxidation of the remaining carbon only 0.18 Torr of carbon dioxide was obtained, corresponding to about 30% of the total carbon. The formation of active carbon on the untreated nickel and the reduced nickel was essentially the same.

G. Oxidized and Reduced Nickel Films.

The H_2 + CO reaction was studied over nickel films oxidized at 673 K and reduced at 773 K (B.4). The results are given in Figure 14 and Table 4. The oxidized and reduced nickel films were less active than the others but were more active than the similarly-treated iron films.

H. Decomposition of carbon monoxide over nickel films.

Decomposition of carbon monoxide (partial pressure 88 Torr) was studied in the presence of helium over untreated and over oxidized and reduced nickel

films. The rate of decomposition was somewhat faster on the untreated nickel films. The deposited carbon on both films was hydrogenated at 673 K. The main product was methane with some ethane (Table 5). Virtually no ethylene was detected. The initial rate of methane formation was greater with the untreated nickel film.

Analysis of the Metal Surfaces by Scanning Electron Microscopy

For each kinetic study using the large plates, small plates for use in the SEM were included in the reactor so that the effect of the reaction on the surface could be observed. Typical micrographs are included in the following pages. The micrographs for iron (A) and for nickel (B) are shown side by side for comparison.

The metal films as formed in the Sputter Coater showed no surface features by SEM (A_1 and B_1). During the course of a reaction (24 hours) as described in A(a) the background surface of the untreated iron film did not change (A_2) while the nickel films showed that the surface had been affected by the reaction (B_2). As observed in A_2 a few irregularly-shaped particles were deposited on the surface. These particles were unaffected by hydrogenation at 673 K for 24 hours, even though most of the carbon was removed by this treatment. These particles might be carbides, oxide or graphitic carbon. The amount was too small for X-ray analysis.

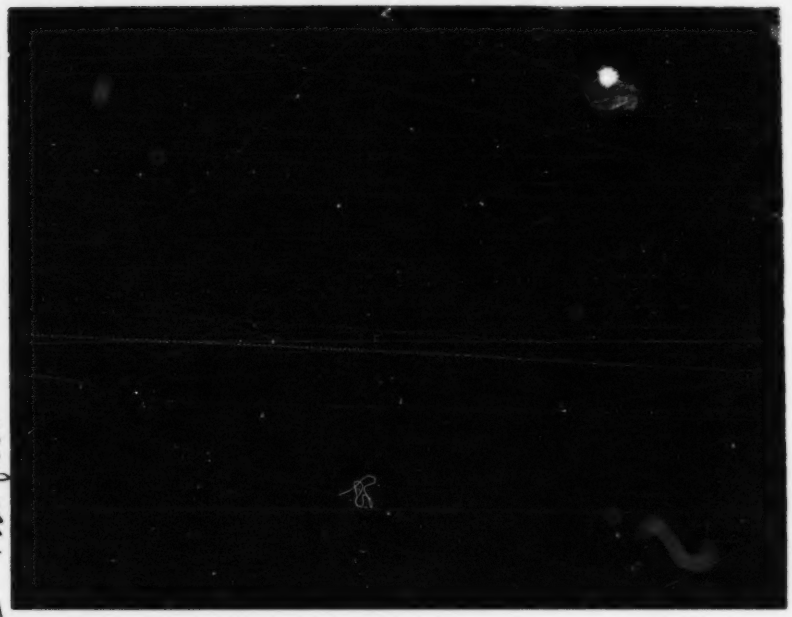
Irregularly-shaped particles were also deposited on the nickel films during the course of reaction, although these appeared somewhat different in shape from the material on the iron surface (B_3 and B_3'). No effect was observed on these particles by the hydrogenation reaction. The particles might be inactive carbon or nickel oxides. Carbide formation during the course of the reaction has been reported in several studies (9,11,12).

Table 5

Decomposition of Carbon Monoxide over Ni Films

	Ni Films	
	Untreated	Oxidized and Reduced
Yield of CO_2 after 24 hours Torr	0.750	0.536
Rate of formation of CO_2, Torr min^{-1}	2.5×10^{-3}	1.36×10^{-3}
Hydrogenation of the carbon on the surface		
Yield of Product Torr		
CH_4	0.348	0.188
C_2H_6	0.003	0.002
Rate of formation of CH_4 Torr min^{-1}	8.3×10^{-3}	4.2×10^{-3}

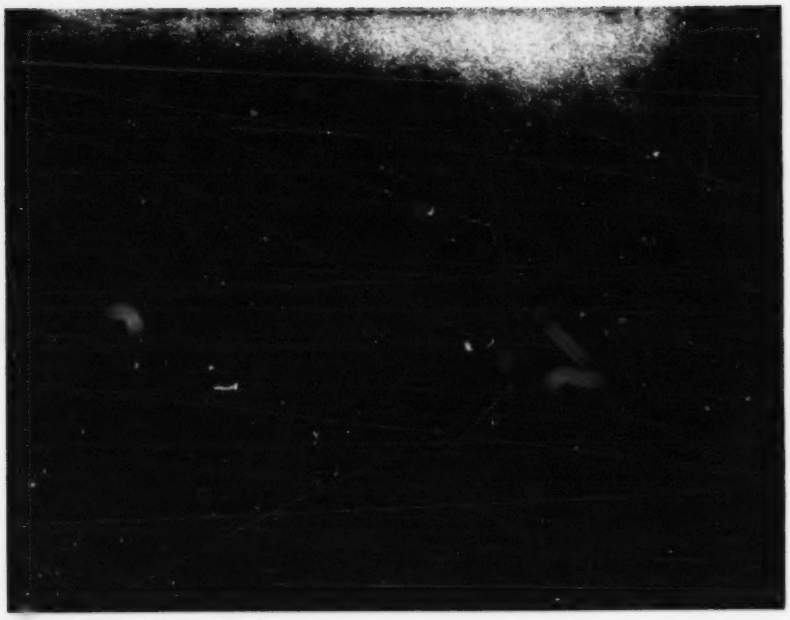
A,



30 µm film

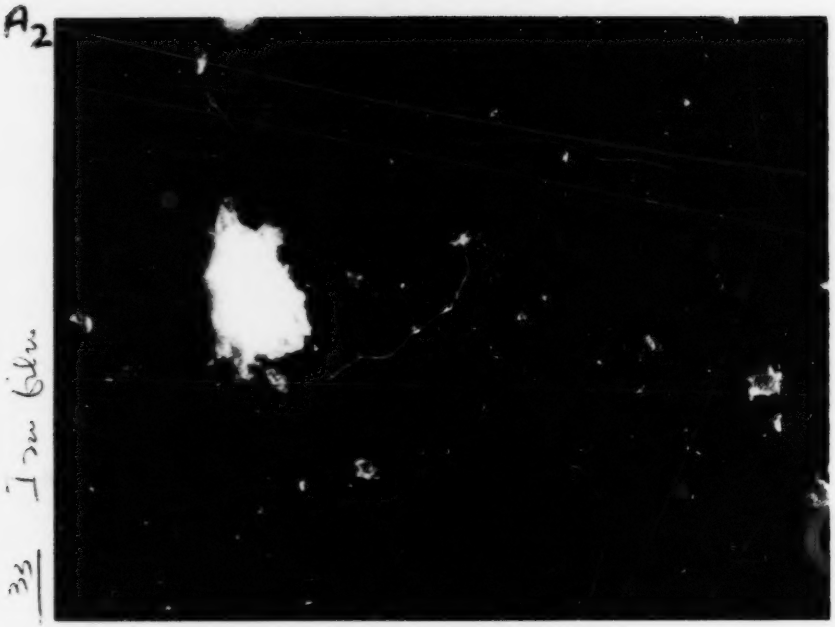
A,

B,



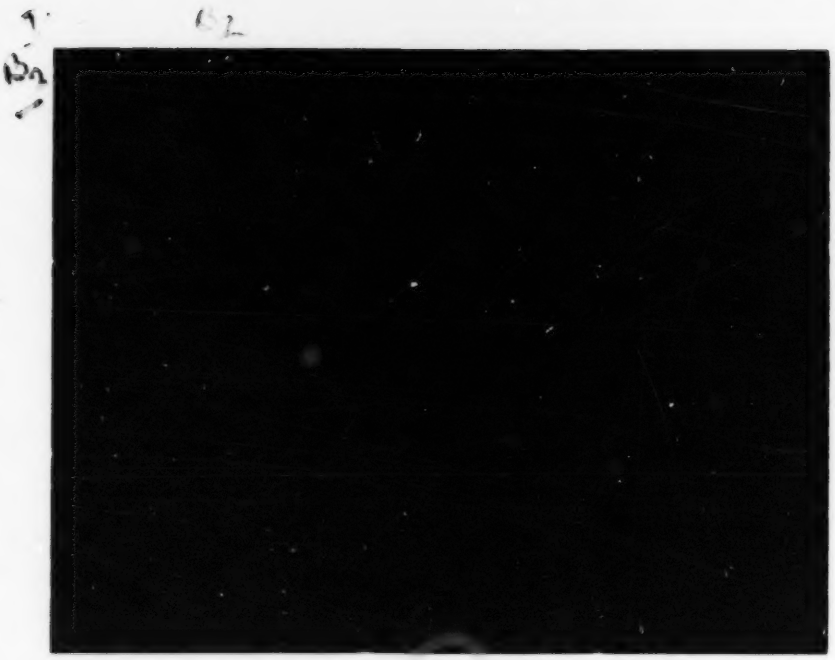
Unbekannt Ni

B,



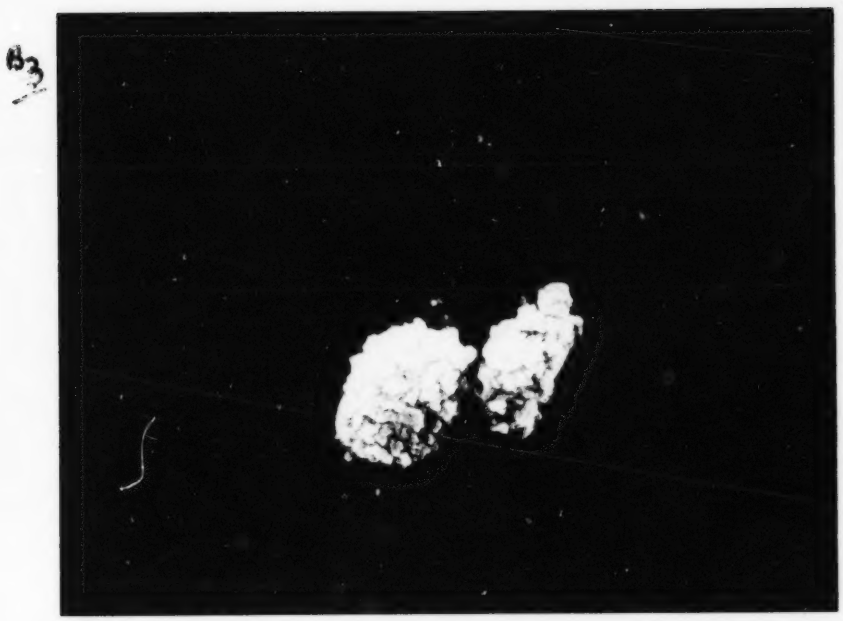
A_2

A_2

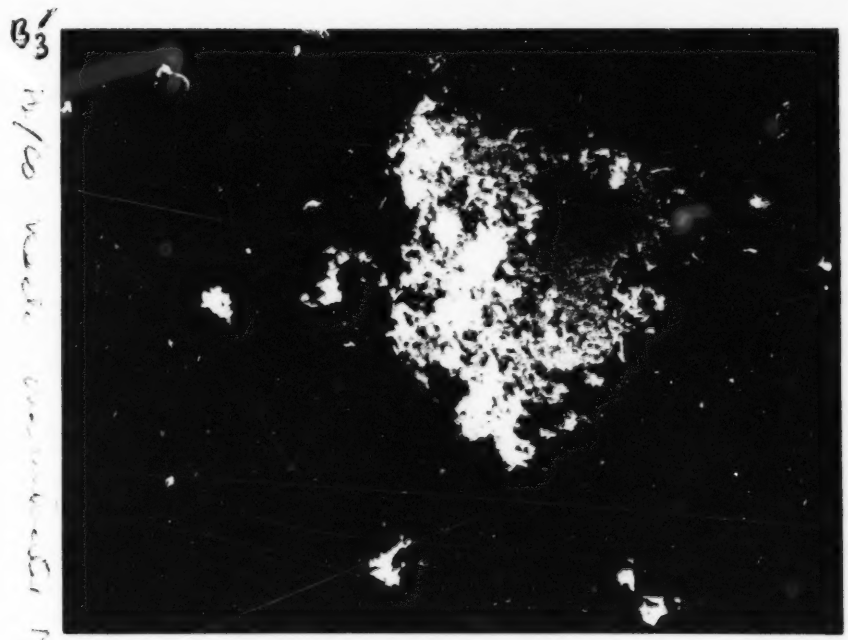


B_2

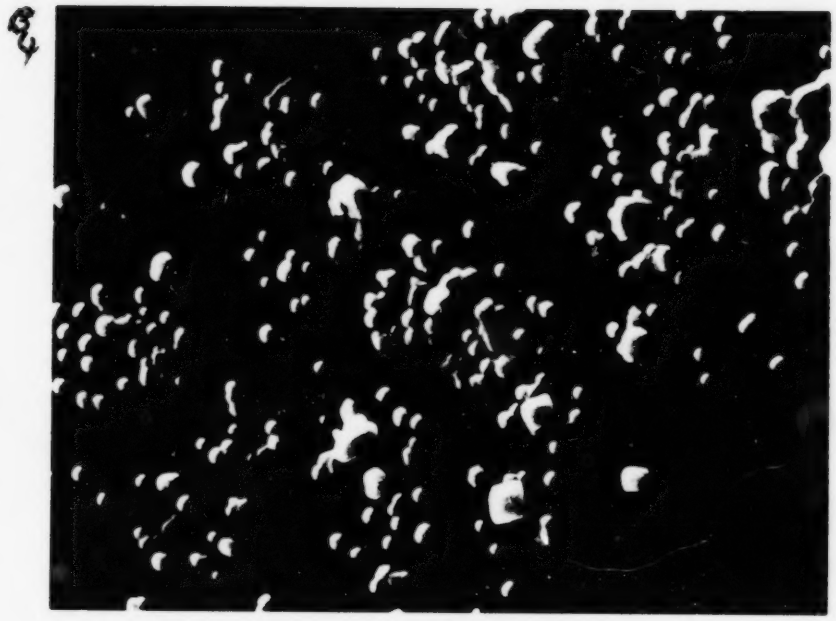
B_2



B_3

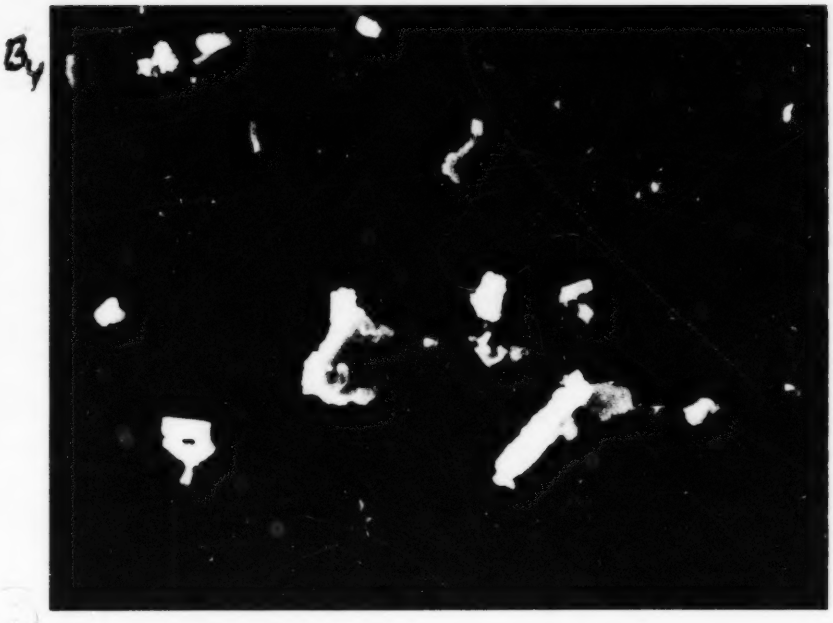


B_3'

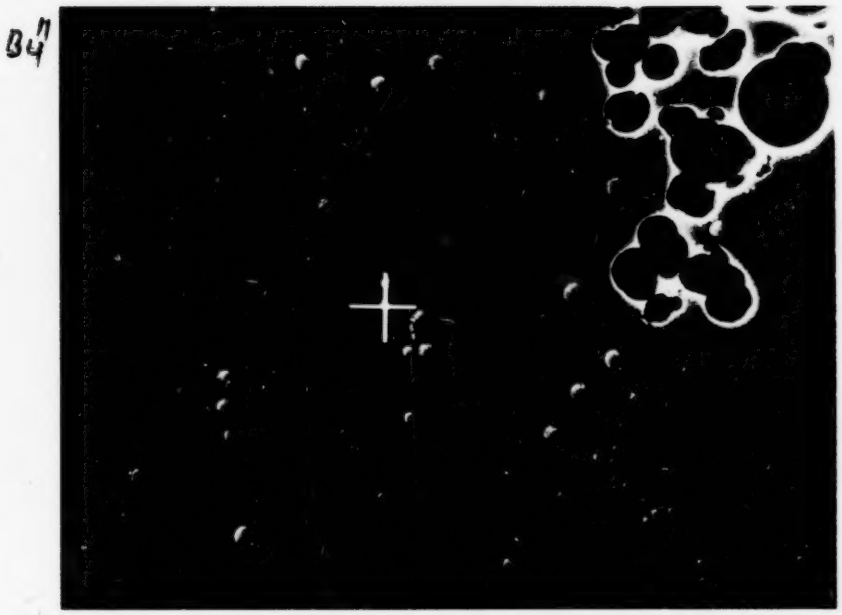


B_4

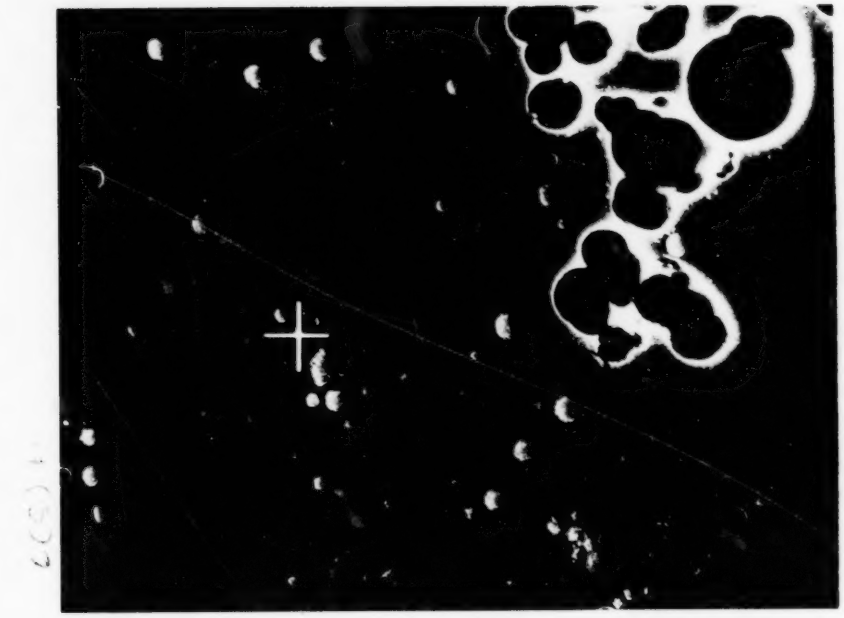
10(6)



B_4'

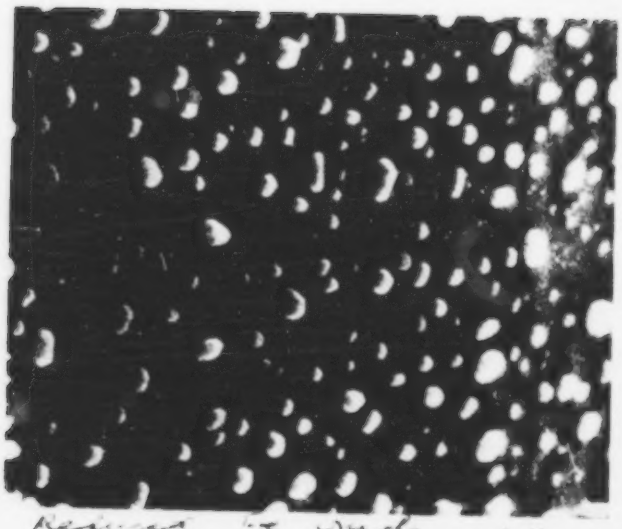


B_4"

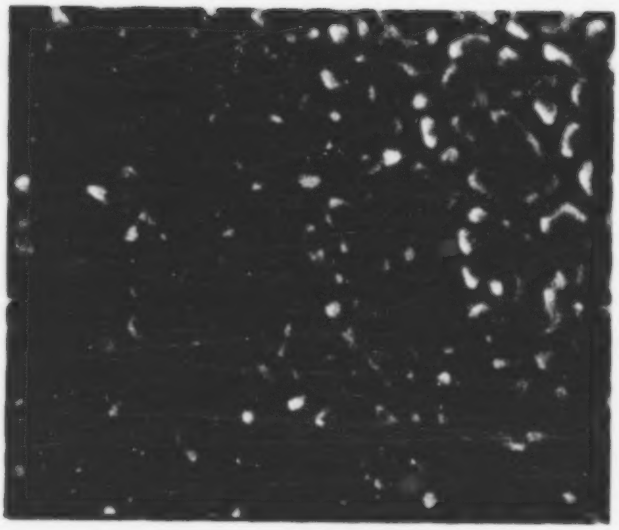


B_4"

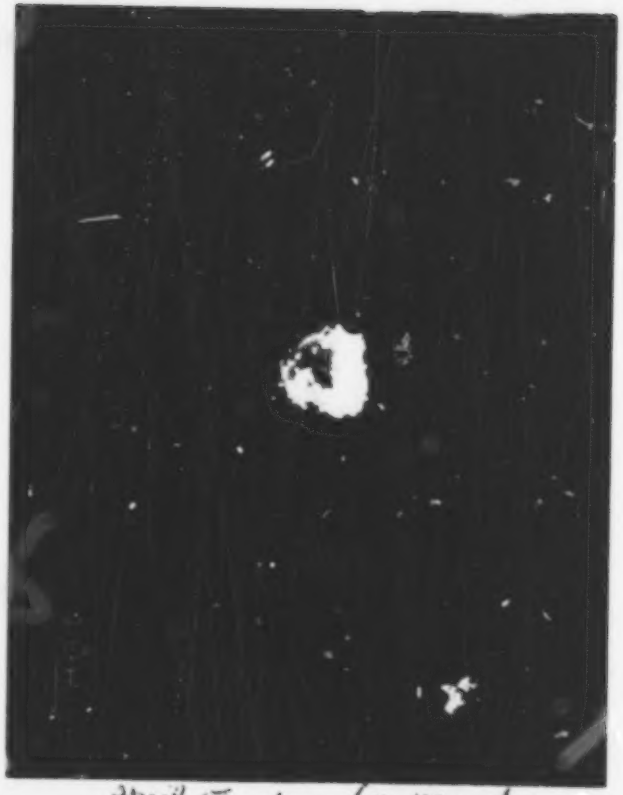
after hydrogenation



H_3



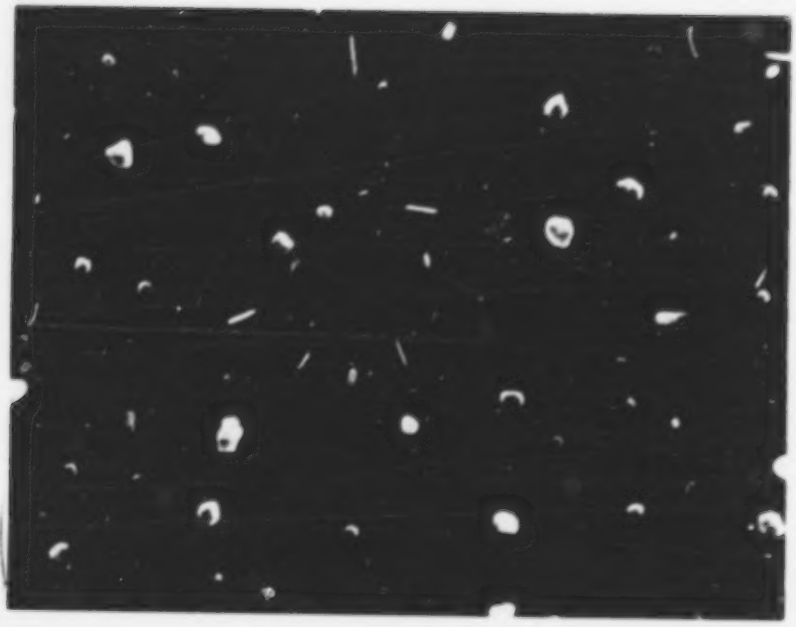
B_5



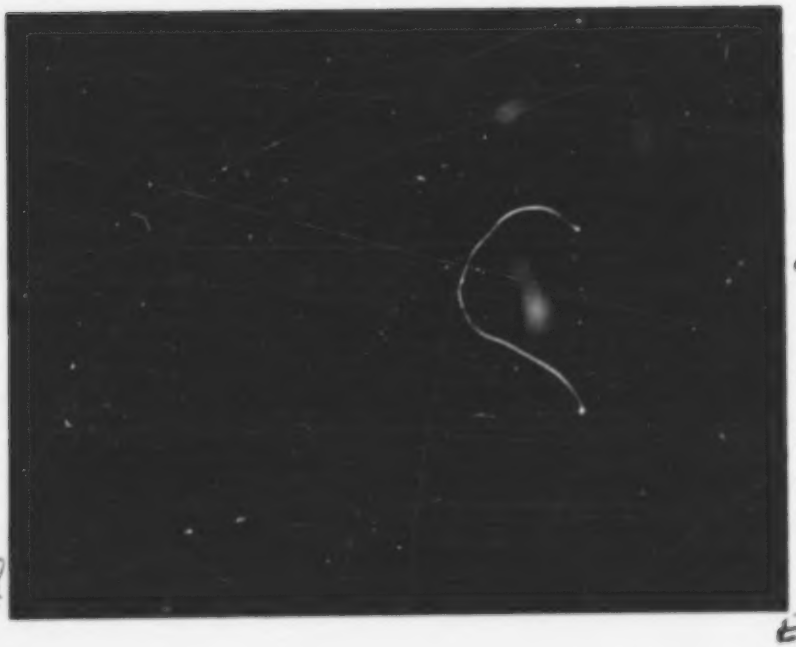
A5

A4

B6



B_6



B_7

#21 Background

When carbon monoxide was decomposed on the metal films no change in the background surface was observed for either metal. Some particle formation, however, was observed. On iron films particles similar to those in A_2 were observed. On nickel a somewhat different type of material was seen (B_4, B_4', B_4''). On heating in hydrogen no appreciable effect on this material was observed. The background surface of the film, however, changed in a manner similar to B_1.

Both iron and nickel surfaces were altered by oxidation-reduction treatment (A_3 and B_5), although the final appearance of each film was quite different. On decomposition of carbon monoxide or reaction of H_2 + CO on the oxidized and reduced films a few particles were observed, similar to those observed on the untreated films. A_4 shows the deposited material from the reaction H_2 + CO over iron films. This material was likewise not affected by treatment with hydrogen.

The oxidation and reduction treatment was separated into an oxidation treatment and reduction treatment in order to ascertain which treatment caused the changes in the surface. On oxidation of iron no appreciable change in the surface structure was observed A_5. Only a few particles were observed on the nickel surface (B_6) and the background was unaltered. On heating the untreated nickel film in hydrogen at 573 for 24 hours the surface no longer appeared smooth and the change was similar to that observed on oxidation and reduction (B_7).

Summary of Results of SEM Analysis of the Metal Films

1. The surface of the untreated nickel film was more affected by the reaction (H_2 + CO) than was the surface of the iron.

2. Both metal surfaces changed on oxidation and reduction treatment, although the appearance of the surface was different in both metals.
3. Reaction with hydrogen effects the surface of the nickel but has no effect on the iron surface.
4. During decomposition of carbon monoxide more particles of regular and irregular shapes were observed on nickel than on iron.

Further observations on the metal films.

After sputtering, the metal films were firmly attached to the plate and could not be disturbed by touching with paper. After carbon deposition the films were darkened, particularly the nickel, and the optical density increased (Figures 2 and 3 in the Appendix). At this stage the nickel film was only loosely bound to the plate and could be cleanly wiped off with paper. This was not the case with the iron film with a carbon deposit. When the carbon was removed from the film by reaction the metal film was left with features similar to the original film. In the case of nickel, the optical density returned to the original value and the film could not be easily removed by rubbing.

These effects suggest that the carbon deposit forms an interstitial compound with nickel to the extent that the bonds of the metal to the quartz are much weakened. The process appears completely reversible.

Discussion

A. Carbon Deposition

The most striking result from the present studies is the absence of any surface structure which may be attributed to carbon deposition. In every reaction which was tested it was shown that carbon was indeed formed on the

surface and could be recovered either by reaction with hydrogen or by oxidation. The amount of carbon was, of course, not large and the thickness of the layer of carbon was estimated as 40 - 100 nm using a density of carbon of 2.1 g mL^{-1}. It must be concluded that the carbon forms in a very uniform layer on the metal surface.

B. Reaction of H_2 + CO

The present results provide some interesting comparisons in reactivity. A summary is given in Tables 6 and 7. The highest rate of methanation was observed on the reduced iron films, although the rate on the untreated iron films was almost the same. The rate of formation of methane on untreated films of nickel was the same as on similar films of iron. Reduction of the nickel film increased the rate, while a slight reduction was observed on similar treatment of the iron films. Oxidation and reduction of the iron film drastically reduced the reactivity, whereas the same treatment of the nickel film caused only a slight reduction. The selectivity for methane was highest on the nickel films.

These comparisons of the rates are qualitative since detailed analyses of each surface were not performed*. It clearly shows, however, that the oxidizing and reducing treatments have quite different effects on the two metals. Reports in the literature are sometimes conflicting regarding the effectiveness of the oxidized or reduced metal. It has been observed that reduced iron has a lower activity and various reasons have been suggested (1,2). The activity of the oxide has been a controversial subject, probably partly because of the variety of surfaces used which contain some form of oxide. Some studies reported a higher activity for the oxide but others suggest that the oxide is inactive and does not

---

*Two films of iron were analyzed in the laboratories of EMR by AES. One film was of untreated iron and showed the presence of oxide as well as an impurity of sulphur.

Table 6

Reaction of H_2 + CO

$H_2/CO = 2$ Total Pressure = 490 Torr T = 573 K

Metal film	Rate of formation of CH_4 Torr min^{-1}	Selectivity of CH_4	SEM analysis	
			Before reaction	After reaction
Iron untreated	2.0×10^{-3}	0.88		
Iron reduced	3.3×10^{-3}	0.82		
Iron oxidized and reduced	inactive			
Iron oxidized	2.2×10^{-3}	0.91		
Nickel untreated	2.1×10^{-3}	0.92		
Nickel reduced	4.2×10^{-3}	0.92		
Nickel oxidized and reduced	0.75×10^{-3}	0.89		

Table 7

Reaction of H_2 + CO

Final products after 24 hours

$H_2/CO = 2$ Total Pressure = 490 Torr T = 573 K

	Pressure of Product, Torr				
Metal film	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8
Iron untreated	3.87	0.021	0.25	0.08	0.05
Iron reduced	2.39	0.135	0.18	0.01	0.01
Iron oxidized and reduced	0.07	traces	traces		
Iron oxidized	0.85	0.02	0.14	0.01	0.01
Nickel untreated	1.40	0.005	0.09	0.003	0.02
Nickel reduced	2.37	0.017	0.15	0.007	0.02
Nickel oxidized and reduced	0.29	0.005	0.13	-	-

chemisorb carbon monoxide effectively. Because we are not certain of the composition of the metal films our results are not conclusive regarding the activity of the oxide.

Reduction of the metal film had a different effect on the nickel than on the iron. For iron the activity was slightly reduced and the surface appeared unaltered. Reduction of the nickel film increased the reactivity and also altered the surface. The increased reactivity therefore may be associated with the change in the morphology of the metal. The effect, however, was not large in either case and would suggest that the presence of oxide on the untreated films was not very important in the over-all reaction.

The most striking effect was the reduction in activity following oxidation and reduction of the metal films, particularly in the case of iron. From a comparison of the micrographs of the films before and after treatment it appears that the change in surface area is probably not sufficient to account for the change in reactivity. Analysis by AES of a sample of the oxidized and reduced film showed that the granules (A_3) contained some oxide enclosed in a shell of metallic iron. This suggests that the pure metal may be inactive and that a certain amount of oxide exposed to the reactants may increase the reactivity.

C. Hydrogenation of the Deposited Carbon

The products from the hydrogenation of the surface carbon were similar to those formed in the reaction except that no olefins were detected. Some controversy exists concerning the role of carbon monoxide in chain growth in the hydrogenation of carbon monoxide. Our results suggest the presence of carbon monoxide is not an essential factor in the formation of higher hydrocarbons (Table 8).

Not all the carbon was sufficiently active to be converted to hydrocarbons at 673 K. The carbon deposited on the nickel surfaces appeared more reactive than that on the iron surfaces. The activity of the carbon was the same on the untreated

Table 8

Hydrogenation of Carbon deposited during reaction H_2 + CO

Pressure of H_2 = 400 Torr T = 673 K

Metal film	Hydrocarbon after 24 hours Torr			Rate of formation of CH_4 Torr min^{-1}	CO_2 after oxidation Torr	% Carbon hydrogenated
	CH_4	C_2H_6	C_3H_8			
Iron untreated	0.582	0.007	0.004	6.6×10^{-3}	0.41	60
Iron reduced	0.491	0.006	0.003	3.7×10^{-3}	0.37	57
Nickel untreated	0.608	0.01	0.007	5.4×10^{-3}	0.22	75
Nickel reduced	0.426	0.008	0.005	4.2×10^{-3}	0.18	72

as on the reduced films. This would suggest that the presence of oxide is not an important factor in the characteristics of the surface carbon formed during the reaction.

D. Decomposition of Carbon Monoxide and Hydrogenation of Surface Carbon

A summary of the results is given in Table 9. The products from the hydrogenation of the carbon formed by decomposition of carbon monoxide alone were not significantly different from the products formed by hydrogenation of the carbon formed as intermediate during the reaction. The selectivity for methane was similar and no olefins were detected. The percentage of the carbon which could be hydrogenated, or the active carbon, was for the untreated Fe film higher than observed from the intermediate carbon, whereas for the Ni film this percentage was lower. The presence of hydrogen in the reactants therefore affects the characteristics of the surface deposit of carbon but the effect is different for the two metals.

For carbon formed by the decomposition of carbon monoxide the percentage active carbon was the same for both iron and nickel. The percentage active carbon formed on the oxidized and reduced metal surfaces was also the same for iron and nickel, even though very much less carbon was formed on the iron film than on the nickel film. This suggests that the very low rate of the reaction over the oxidized and reduced iron film is caused by a low rate of formation of carbon and not by a particularly inactive form of carbon.

E. Characteristics of the Metal Surfaces

The smooth surface of the nickel film was more easily altered both by the reaction (H_2 + CO) and by reduction with hydrogen than was the iron film. The percentage active carbon formed on nickel was significantly greater when the carbon was formed in the presence of hydrogen than in its absence. The role of hydrogen

Table 9

Decomposition of CO and Hydrogenation of Carbon

Pressure of CO = 83 Torr Pressure of H_2 = 500 Torr

Pressure of Hc = 400 Torr T = 673 K

T = 573 K

Metal film	CO_2 after 24 hours	Products of hydrogenation after 24 hours, Torr		% Carbon hydrogenation
	Torr	CH_4	C_2H_6	
Iron untreated	0.50	0.45	0.008	90
Iron oxidized and reduced	0.07	0.027	0.002	45
Nickel untreated	0.75	0.35	0.003	45
Nickel oxidized and reduced	0.54	0.19	0.002	40

therefore seems somewhat more important in reactions over nickel than over iron. Many explanations for such an effect are possible, relating, for example to properties of the oxide on the surface or different characteristics of a carbide intermediate. The particles observed as deposits on both metals could not be identified except that they are unlikely to be carbon.

Despite some of the similarities in the reactions on iron and nickel as shown by the results here, a major kinetic difference, reported many times, was also apparent in these reactions. An induction period was observed in the reaction on iron while none was observed in the reaction on nickel. Although some explanations have been suggested, usually in terms of the formation of intermediate carbides, none seems entirely satisfactory. The present results do not, however, provide firm evidence which would allow a further explanation or interpretation of this effect.

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APPENDIX

Calibration Factors for Gas Chromatographic Analysis

Pressure in sampler (1cc) = Pressure in Reaction Vessel

Product	Peak Height / Pressure in sampler (Torr)	Detector
CH_4	1.5×10^4	FID
C_2H_6	4.9×10^3	FID
C_2H_4	6.5×10^3	FID
C_3H_8	8.2×10^2	FID
CO_2	14	TC

Captions for Figures

1. Optical density as a function of the weight of iron in the film.
2. The optical density of the iron films as a function of wave length.
   ○ : blank;
   x : Fe film untreated;
   □ : Fe film oxidized
3. The optical density of the nickel films as a function of wave length.
   O : blank;
   □ : Ni film untreated;
   x : Ni film oxidized

Fig. 1

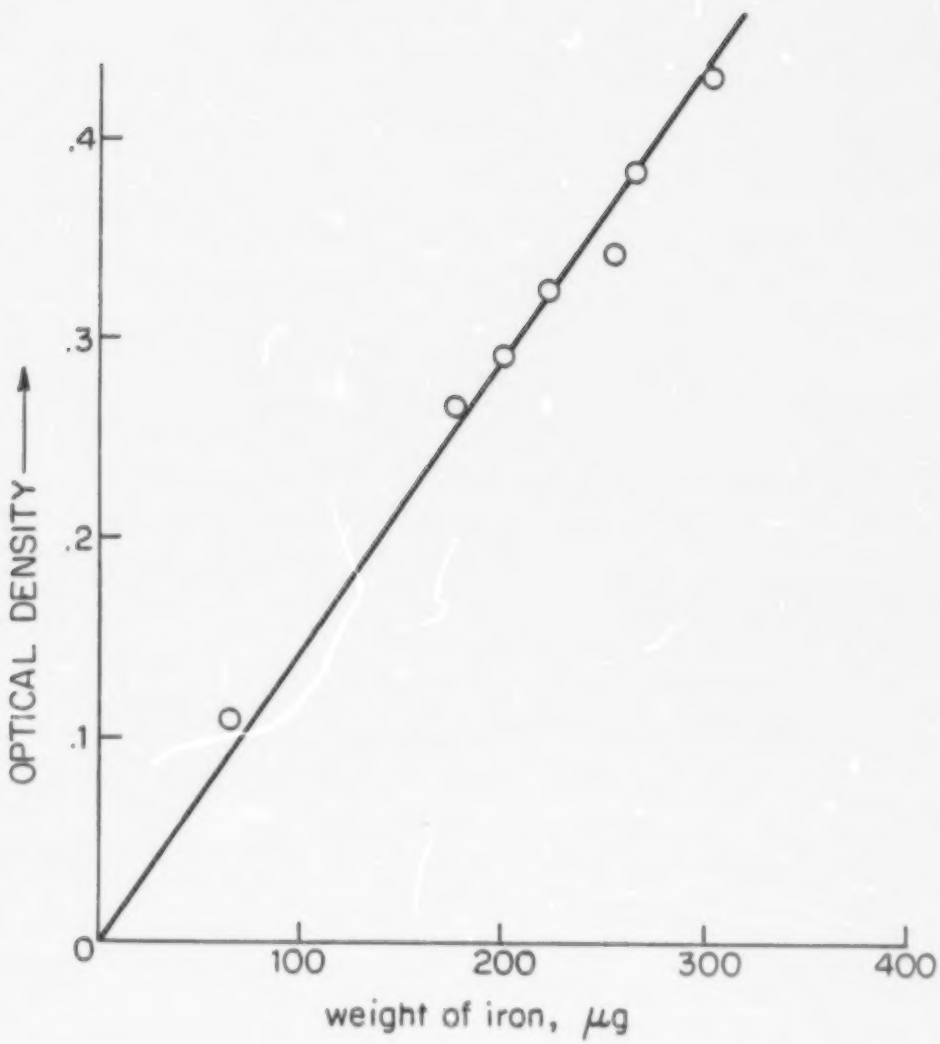


Fig. 2

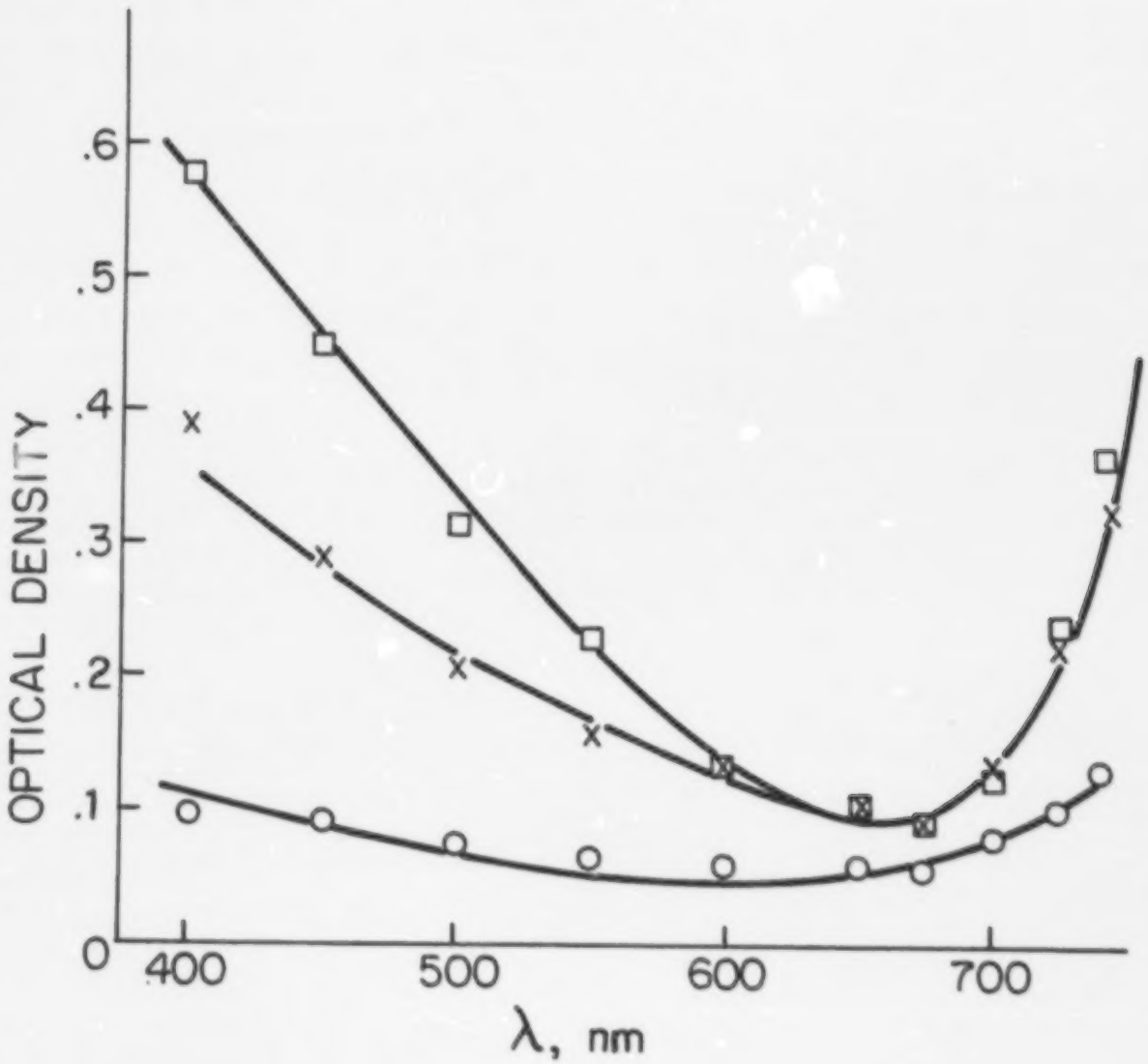
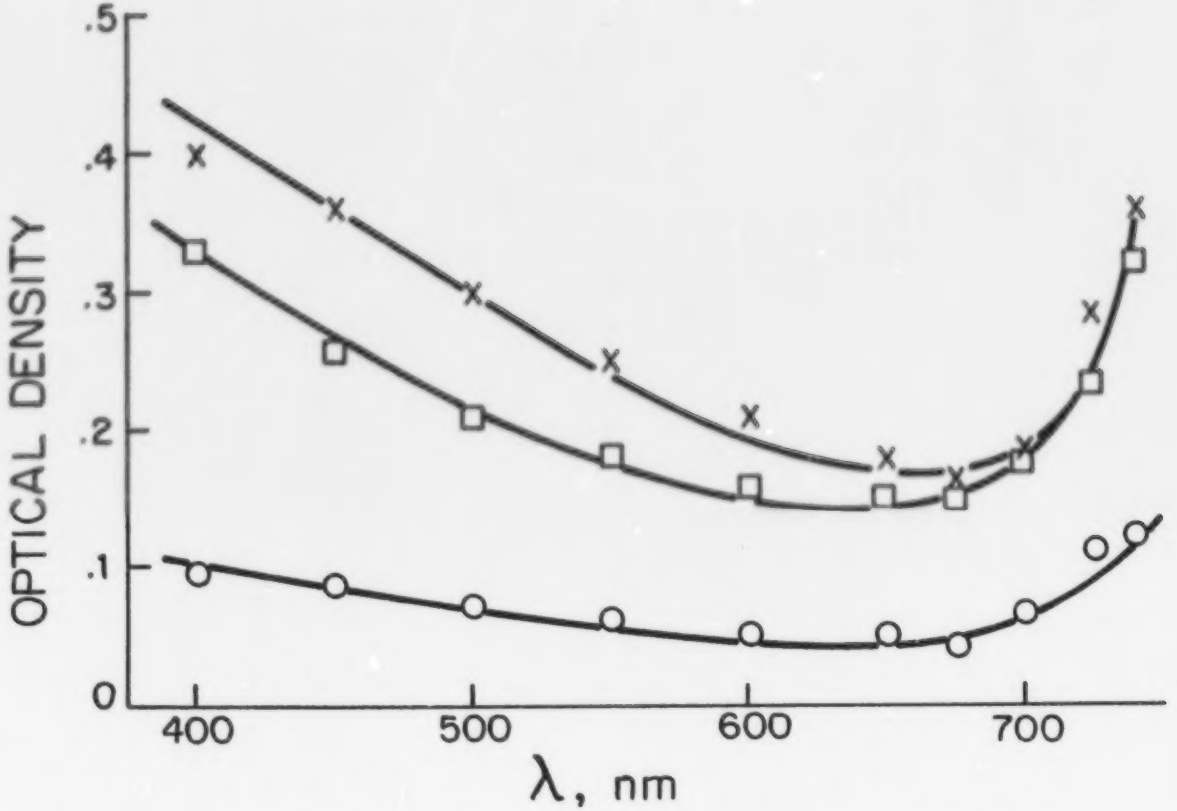


Fig. 3



Report on Additional Task for Contract 03ST-23440-3-9161

"Carbon Deposit Morphology on Metal Surfaces during Hydrocarbon Synthesis"

K.C. Khulbe and M.H. Back

EEFECT OF CARBON ACCUMULATION ON THE INDUCTION PERIOD

Introduction

The purpose of the experiments described here was a comparison of the induction period observed during the reaction of hydrogen and carbon monoxide over an iron catalyst with the induction period observed in the reaction of hydrogen with carbon previously deposited on an iron surface by the decomposition of carbon monoxide. The results of the studies described in the main report showed that in the reaction of hydrogen and carbon monoxide over the iron catalyst an induction period was always observed. It was shown, however, that the induction period was reduced by allowing the intermediate carbon to accumulate between reactions. After several treatments the induction period reached a small limiting value and was not further reduced. On the other hand, in the reactions of hydrogen with carbon no induction period was observed under the conditions used for the reaction. In comparing these two systems then, on the one hand, the reaction of hydrogen and carbon monoxide over iron catalyst where carbon has accumulated during a series of reactions, and on the other hand, the reaction of hydrogen with carbon deposited by decomposition of carbon monoxide, it appeared that the characteristic induction period observed in the first case was not present in the second case. The conditions (temperature and pressure) for the hydrogenation of carbon, the second case,

were, however, different from those used for the reaction of hydrogen and carbon monoxide and these differences could account for the different kinetic characteristics of the reaction. The present sets of experiments were designed to test the kinetic characteristics with respect to the induction period of the reaction of hydrogen and carbon monoxide in the presence of accumulated carbon and the reaction of hydrogen with deposited carbon under identical conditions. These results thus allow a comparison of the reactivity of carbon formed by decomposition of carbon monoxide in the presence and absence of hydrogen.

Experimental

Sets of quartz plates were prepared with a thin film of iron as described earlier. The weight of iron was about 32 g cm^{-2}. The apparatus was as described previously and the procedure and method of analysis were also the same.

Results

Three sets of experiments were performed. The first set was similar to that described under Results A(b), p. 12. A series of consecutive reactions was performed (total pressure 480 Torr, H_2/CO 55, 573 K) with reactants and products removed after each stage but the deposited carbon allowed to accumulate on the catalyst. Four such stages were performed and the results are shown in Figures 1 and 2. As observed previously accumulation of carbon during the induction period reduced the induction period for the following stage until the third stage, after which no further reduction took place. This trend was observed for the C_2 products as well.

Keeping the same catalyst, reactants and products were removed and hydrogen was introduced. The hydrogenation was followed for 30 minutes and the yield of methane is shown in Figure 3A. These results show an induction period of the same magnitude as observed in the reaction after stage IV. The hydrogen was then removed and the carbon was oxidized with 500 Torr of air at 800 K for two hours. The yield of carbon dioxide from this treatment was undetectable. It should be noted that a yield of carbon dioxide comparable to the yield of methane would not have been measurable by our method.

This set of experiments was repeated with conditions the same except for the ratio of hydrogen to carbon monoxide, which was equal to 2. The results (Figure 4 and 5) were comparable to the first set and the hydrogenation reaction (Figure 3B) again showed an induction period of the same length as observed during the reaction of hydrogen and carbon monoxide. In this set the hydrogenation was allowed to proceed until the yield of methane reached its maximum value. Again, oxidation of the remaining carbon produced no detectable carbon dioxide. It may not be concluded, however, that the hydrogenation reaction removed all the carbon, only a substantial portion.

In the second and third set of experiments carbon was first deposited on the catalyst by decomposition of 470 Torr of carbon monoxide for one hour at 573 K. It was estimated that the amount of carbon formed should be comparable to the amount formed during the reaction described in the first set of experiments. For the second set of experiments the rate of the reaction was measured under the same conditions as described in the first

set (total pressure 480 Torr, H_2/CO = 55, 573 K). The yields of products as a function of time are given in Figure 6. The induction period for formation of methane is a little shorter, but similar to that observed in the first set. The yield of ethylene was greater than that of ethane whereas in the previous set the yield of ethane was usually greater than ethylene. Both products are less than 20% of the total.

For the third set of experiments the carbon deposit was hydrogenated with a mixture of hydrogen and helium (total pressure 480 Torr, H_2/He = 55, 573 K). The yields of products as a function of time are shown in Figure 7. The rate of formation of methane was much lower than observed during the reaction of a mixture of hydrogen and carbon monoxide, but was greater than measured from the hydrogenation described in the first set. Ethane and ethylene were also formed as minor products. In this reaction the ethylene yield decreased rapidly after a maximum value at about 20 minutes, indicating secondary hydrogenation to ethane. This appears to be more important in the absence of carbon monoxide, probably because the catalyst surface is available for adsorption of hydrogen.

Two further experiments were performed as a check on the previous studies. A reaction was performed (total pressure 480 Torr, H_2/CO = 2, 573 K) using a film of iron reduced with hydrogen (323 Torr, 573 K, 24 hours). An induction period was observed, similar to that found with the untreated iron film, but the rate was reduced by about a factor of five (Figure 8). A similar reaction was performed using a film of iron oxidized at 800 K with 500 Torr of air for 2 hours. Reaction was negligible even after several hours. These two results substantiate the results of similar experiments performed earlier.

Conclusions

The results of these experiments show that in the hydrogenation of carbon at 573 K on an iron catalyst an induction period of several minutes is observed, whether the reactant is hydrogen alone or in a mixture of hydrogen and carbon monoxide. The induction period is longer with the reactant mixture of hydrogen and carbon monoxide and in the absence of any previous deposit of carbon. That carbon is an intermediate in the formation of methane from the reaction of hydrogen and carbon monoxide is generally agreed and is consistent with the observation of the reduction in the induction period with accumulation of carbon on the catalyst. The fact that the induction period was not reduced to zero in the first set of experiments and was still observed even when carbon was deposited before the start of the reaction shows that formation of carbon is not the only factor contributing to the induction period. As well, the description of the intermediate as carbon is over-simplified. It may be that a particularly active and fleeting form of carbon must develop before the hydrogenation process can begin. Alternatively, the factors leading to the rapid increase in rate may be associated with the series of consecutive C-H bond formation processes which lead to the formation of methane. This sequence of surface reactions has not been fully clarified. Even in the presence of active carbon the hydrogenation may involve a further slow process which leads to the observation of an induction period. Further studies on this problem are essential and kinetic measurements can play a major role in understanding the details of the formation of methane.

Captions for Figures

1. Yield of methane as a function of time during four stages of reaction. Total pressure 480 Torr. Temperature 573 K. Ratio $H_2/CO = 55$.

2. Yields of ethane and ethylene as a function of time during four stages of reaction. Total pressure 480 Torr. Temperature 573 K. $H_2/CO = 55$.

3. Yield of methane as a function of time in the hydrogenation of the carbon produced during the four stages of reaction.

   A. First set of reactions $H_2/CO = 55$

   B. Second set of reactions $H_2/CO = 2$

4. Yield of methane as a function of time during four stages of reaction. Conditions as in Fig. 1 except $H_2/CO = 2$.

5. Yields of ethane and ethylene as a function of time during four stages of reaction. Conditions as in Fig. 2 except $H_2/CO = 2$.

6. Yields of products from the reaction of H_2 + CO over a deposit of carbon. Total pressure 480 Torr. Temperature 573 K. Ratio $H_2/CO = 55$.

7. Yields of products from the hydrogenation of a carbon deposit. Total pressure 480 Torr. Temperature 573 K. Ratio $H_2/He = 55$.

8. Yields of products as a function of time from the reaction of H_2 + CO over a film of iron reduced with hydrogen. Total pressure 480 Torr. Temperature 573 K. Ratio $H_2/CO = 2$.

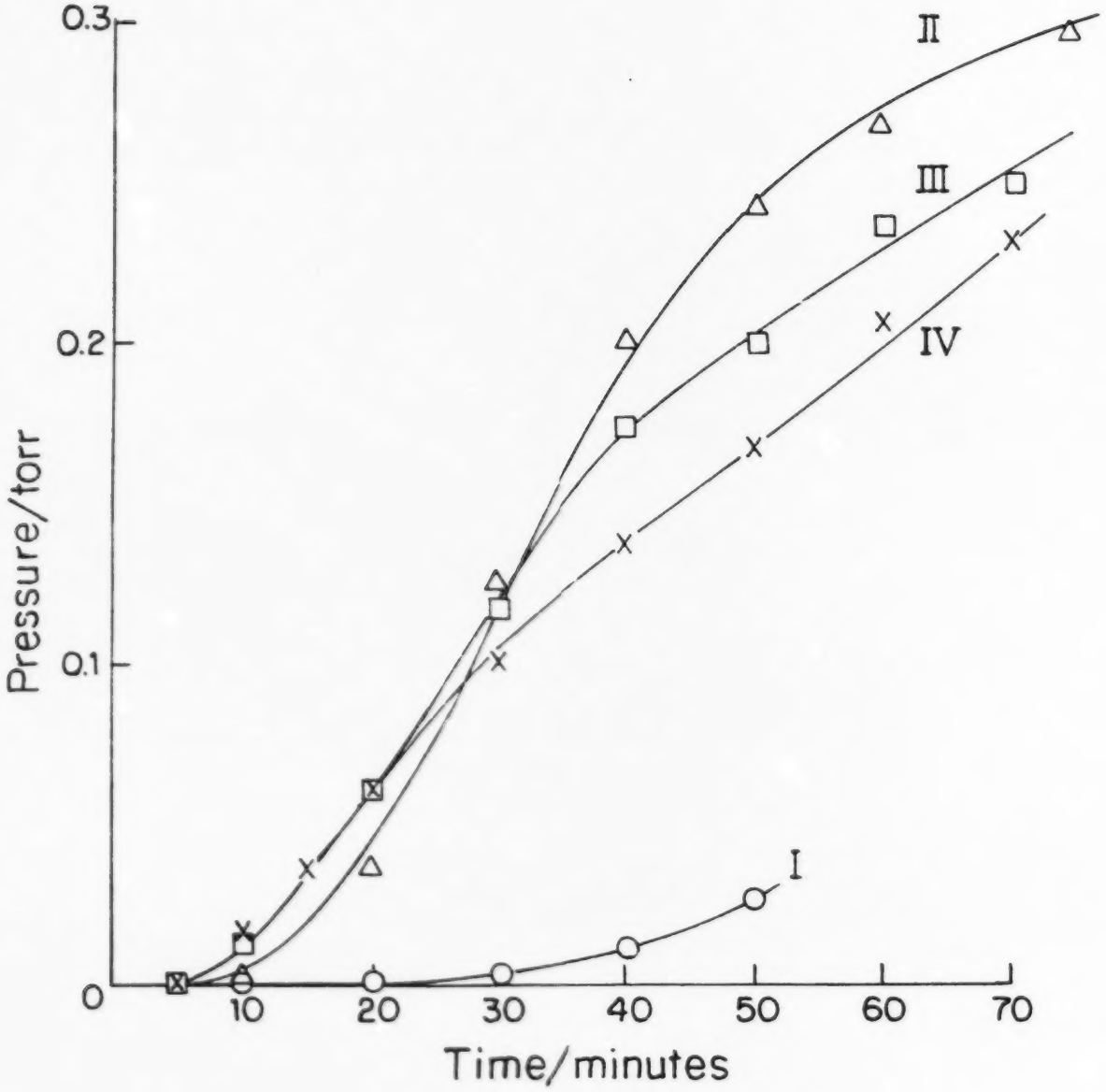

0.3
0.2
0.1
0
Pressure/torr
10
20
30
40
50
60
70
Time/minutes
I
II
III
IV

FIGURE 1

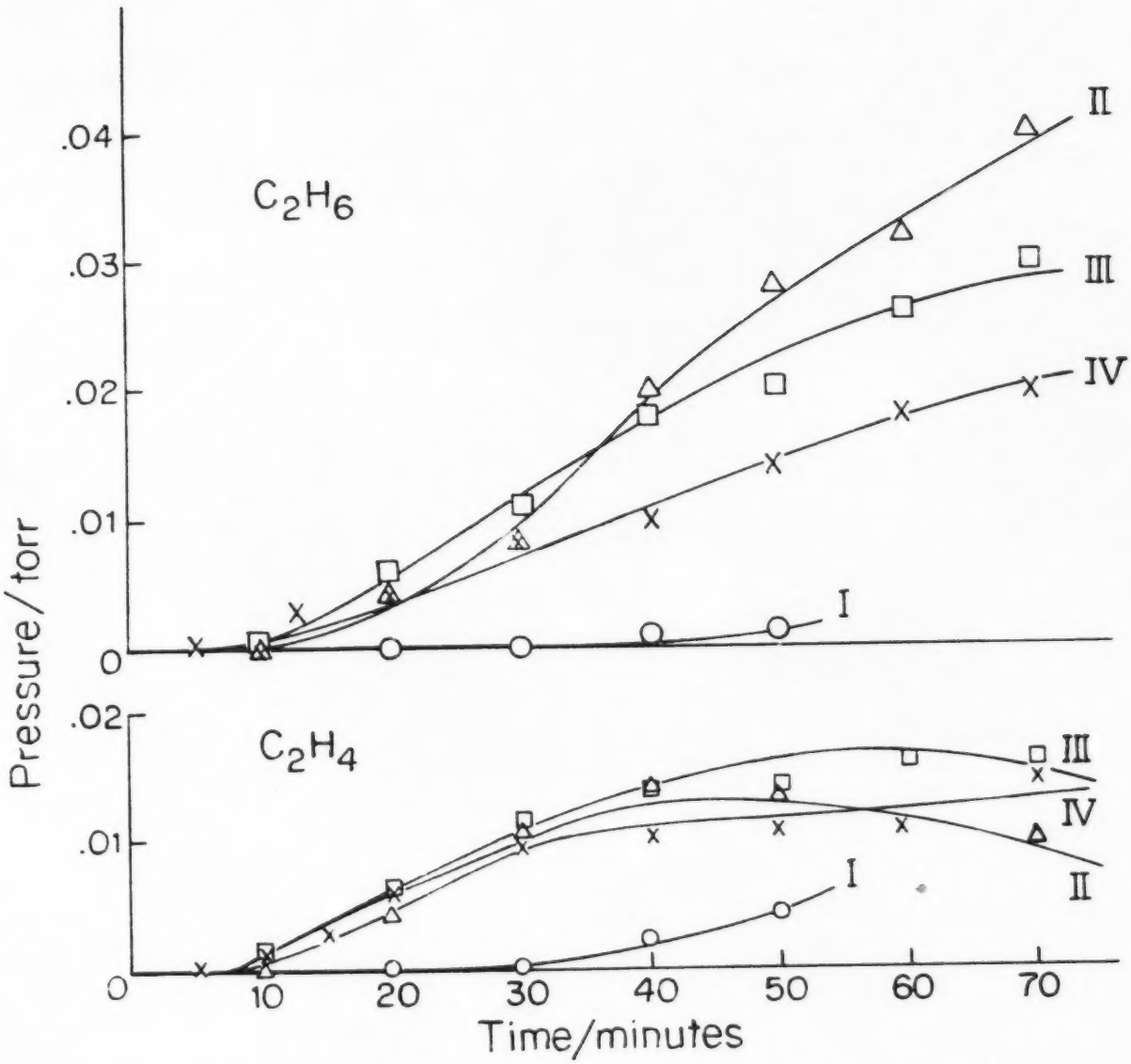

.04
.03
.02
.01
0
C_2H_6
II
III
IV
I
.02
.01
0
C_2H_4
III
IV
II
I
10
20
30
40
50
60
70
Pressure/torr
Time/minutes

FIGURE 2

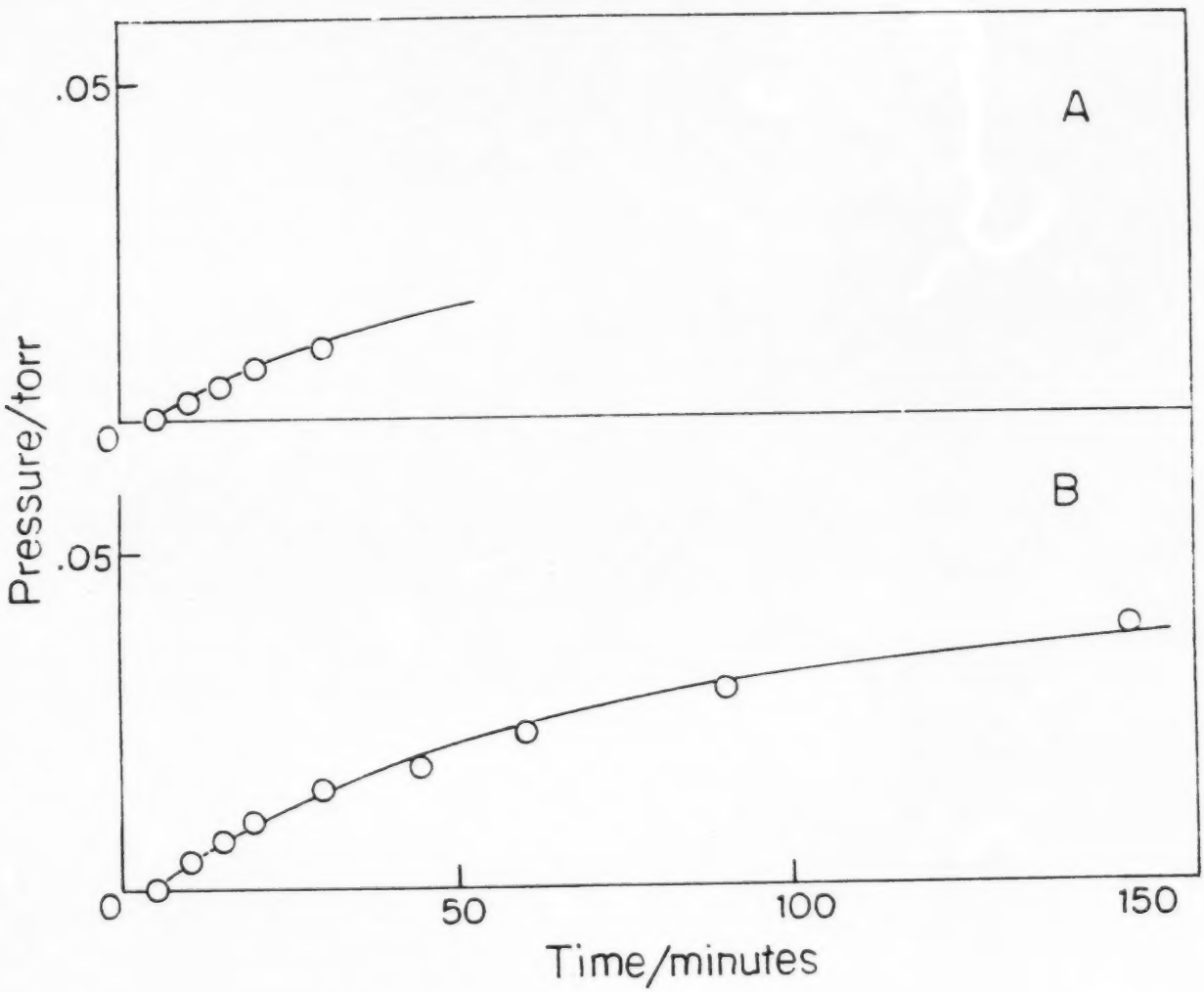


FIGURE 3

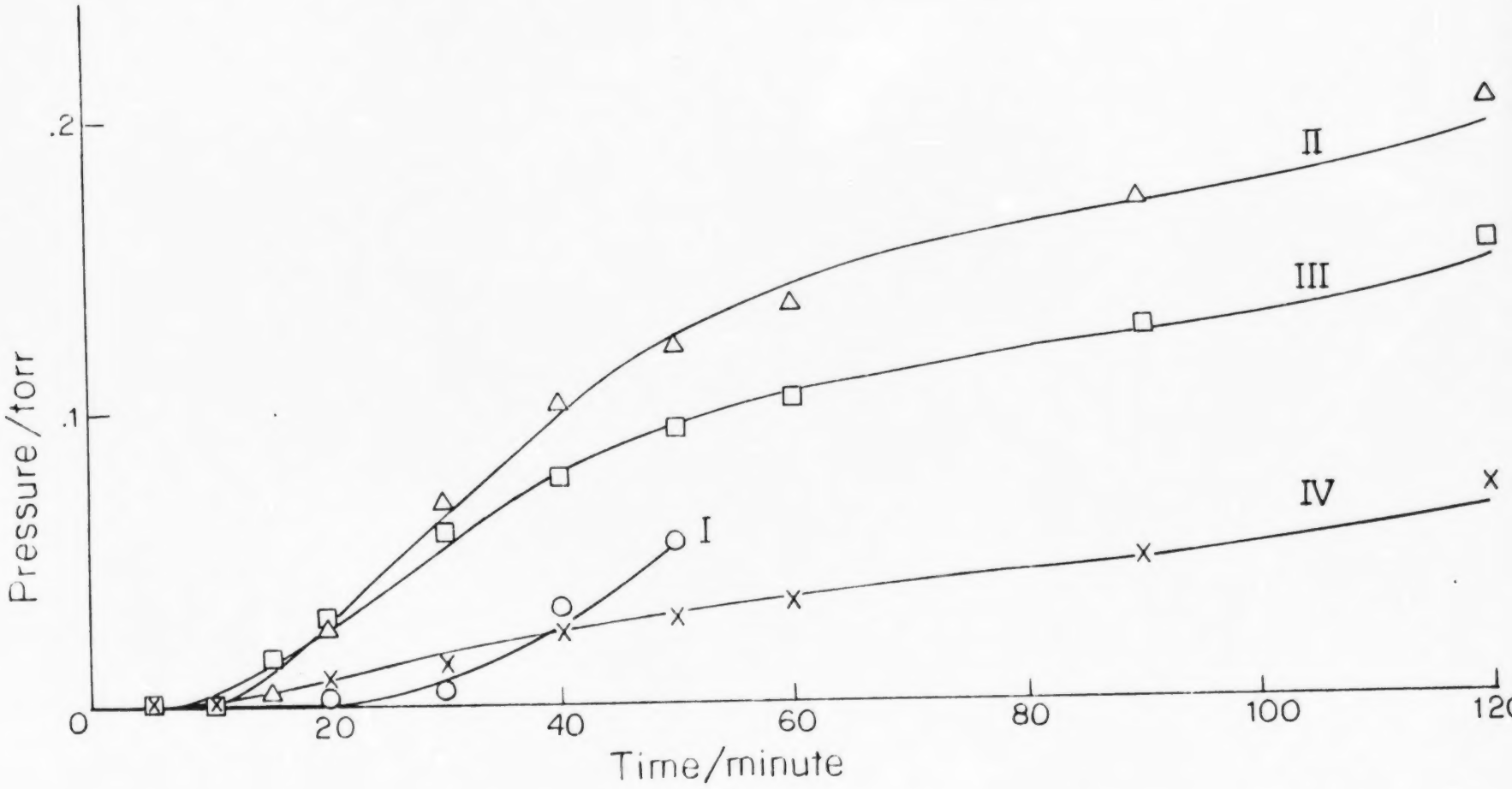


FIGURE 4

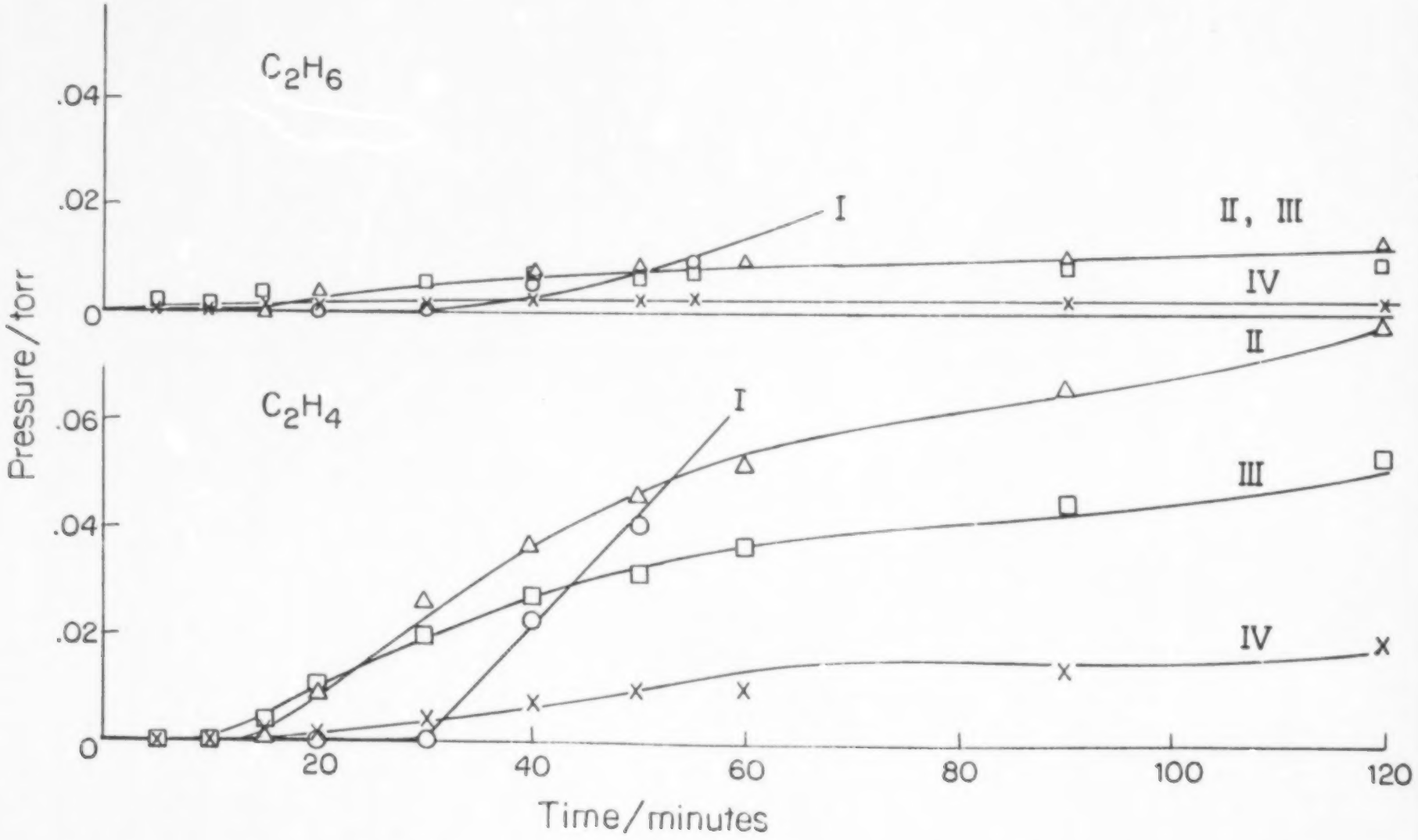

C_2H_6
.04
.02
0
I
II, III
IV
C_2H_4
.06
.04
.02
0
I
II
III
IV
x
20
40
60
80
100
120
Pressure/torr
Time/minutes

FIGURE 5

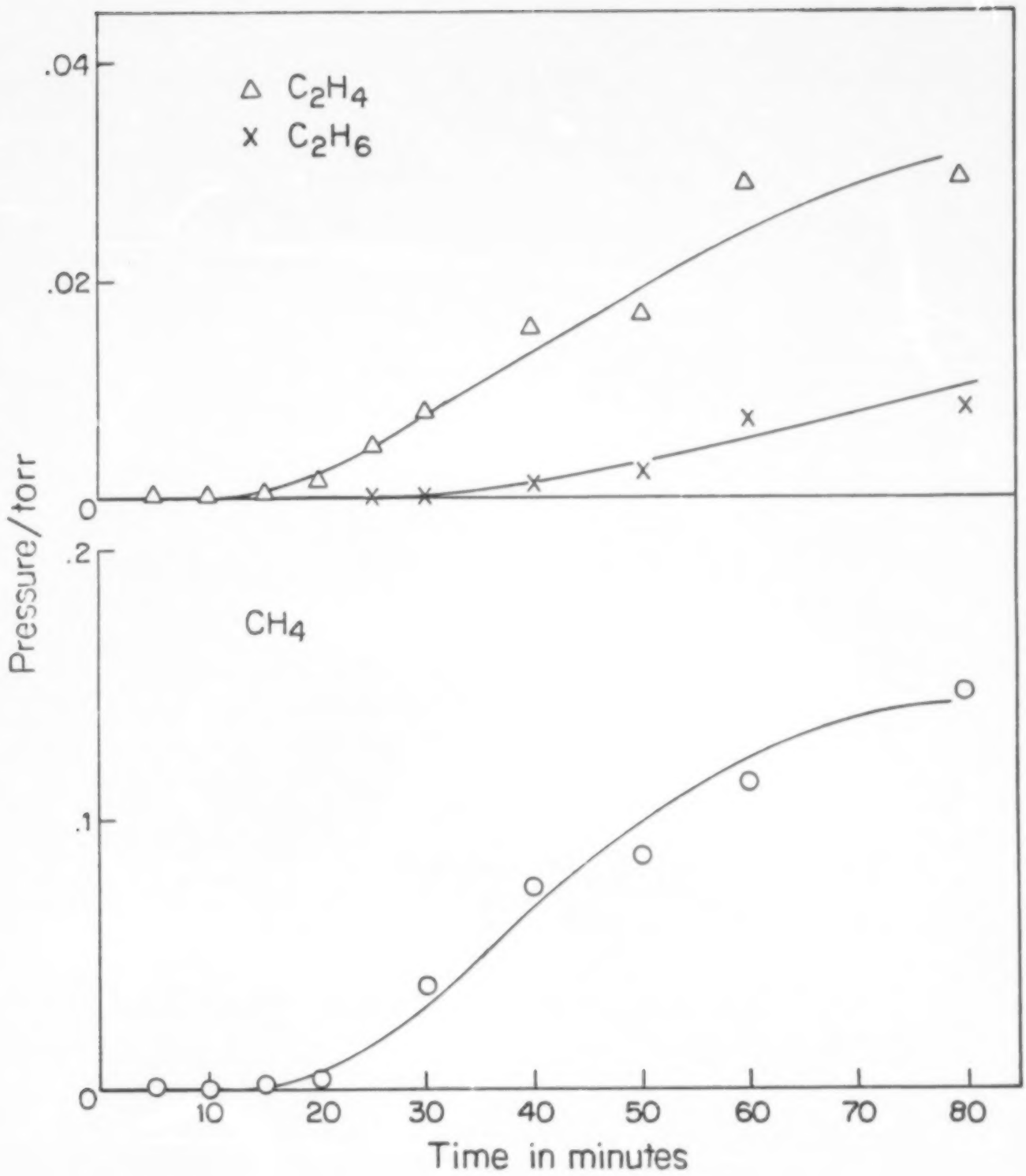

.04
.02
0
.2
.1
0
Pressure/torr
△ C_2H_4
x C_2H_6
CH_4
10
20
30
40
50
60
70
80
Time in minutes

FIGURE 6

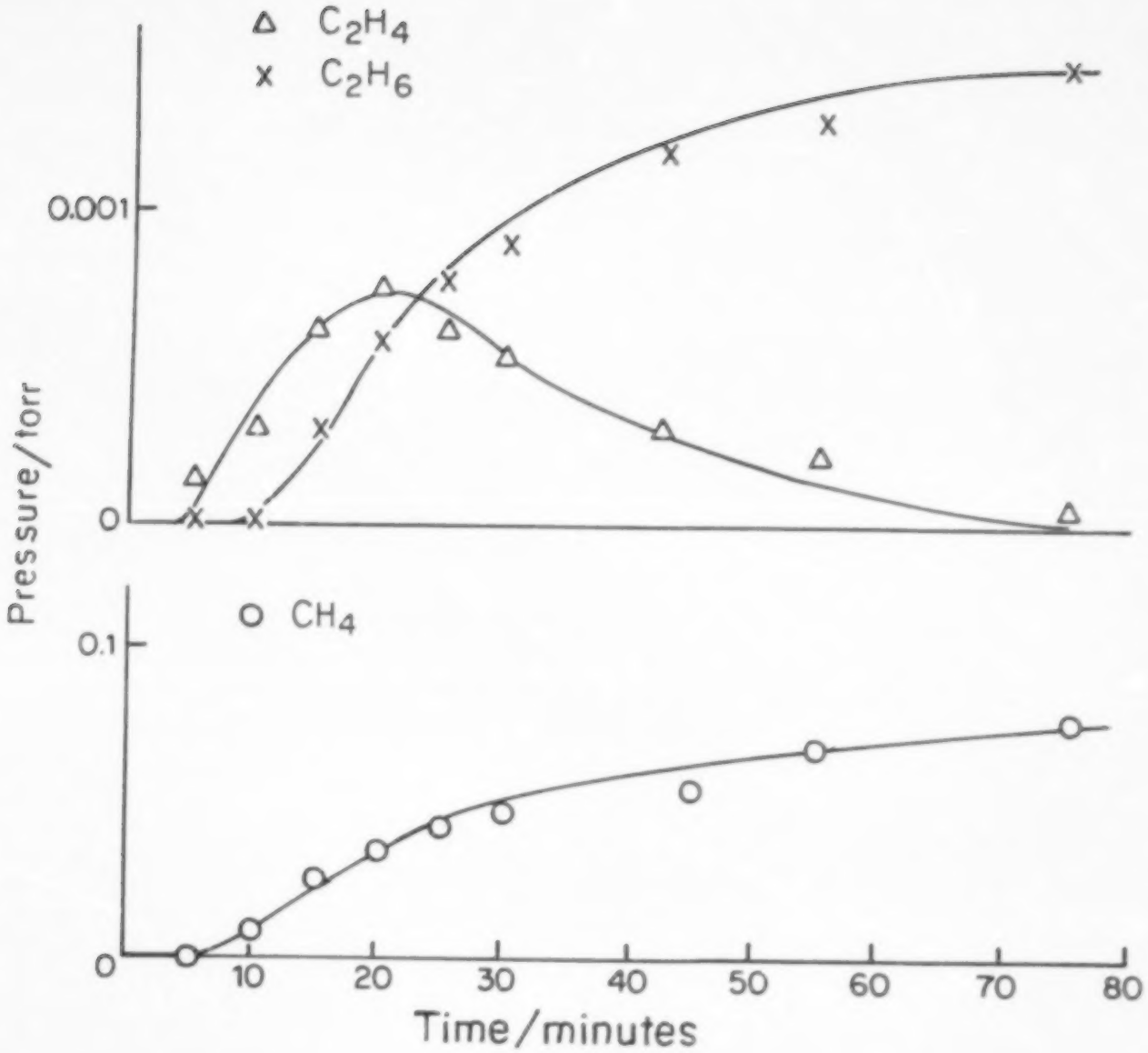
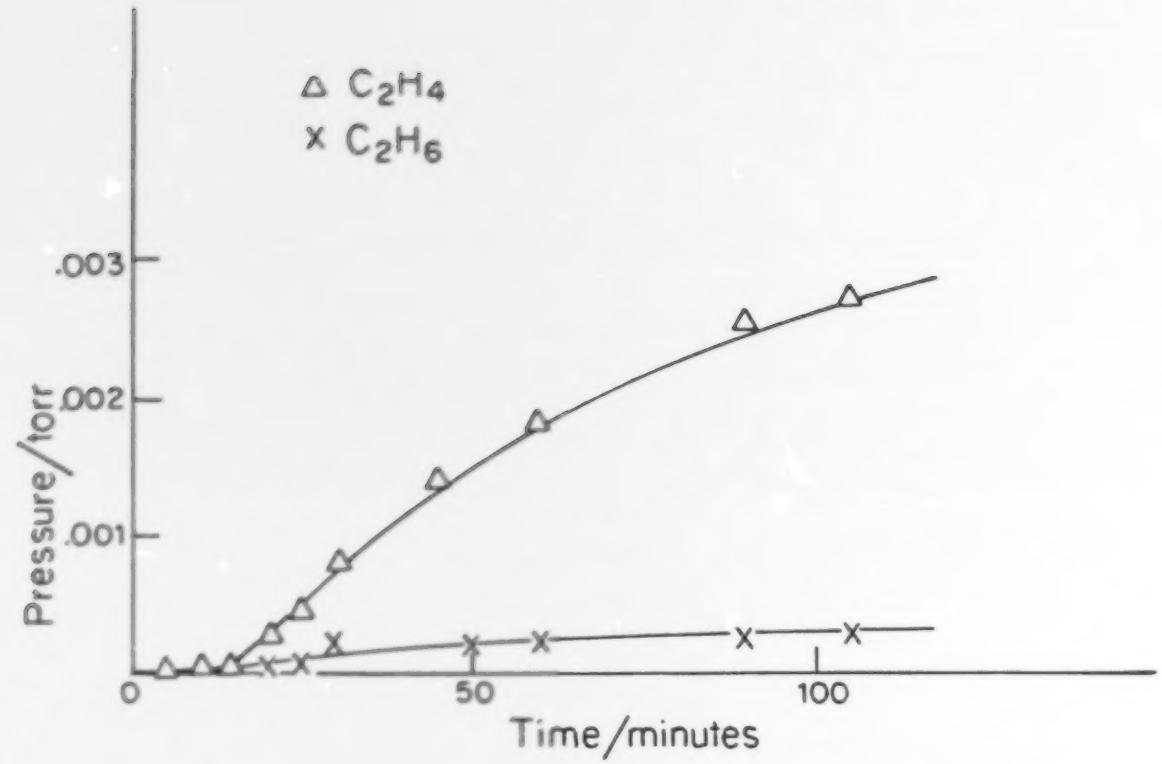

Δ C_2H_4
x C_2H_6
0.001
0
Pressure/torr
O CH_4
0.1
0
10
20
30
40
50
60
70
80
Time/minutes

FIGURE 7


△ C_2H_4
x C_2H_6
.003
.002
.001
Pressure/torr
0
50
100
Time/minutes

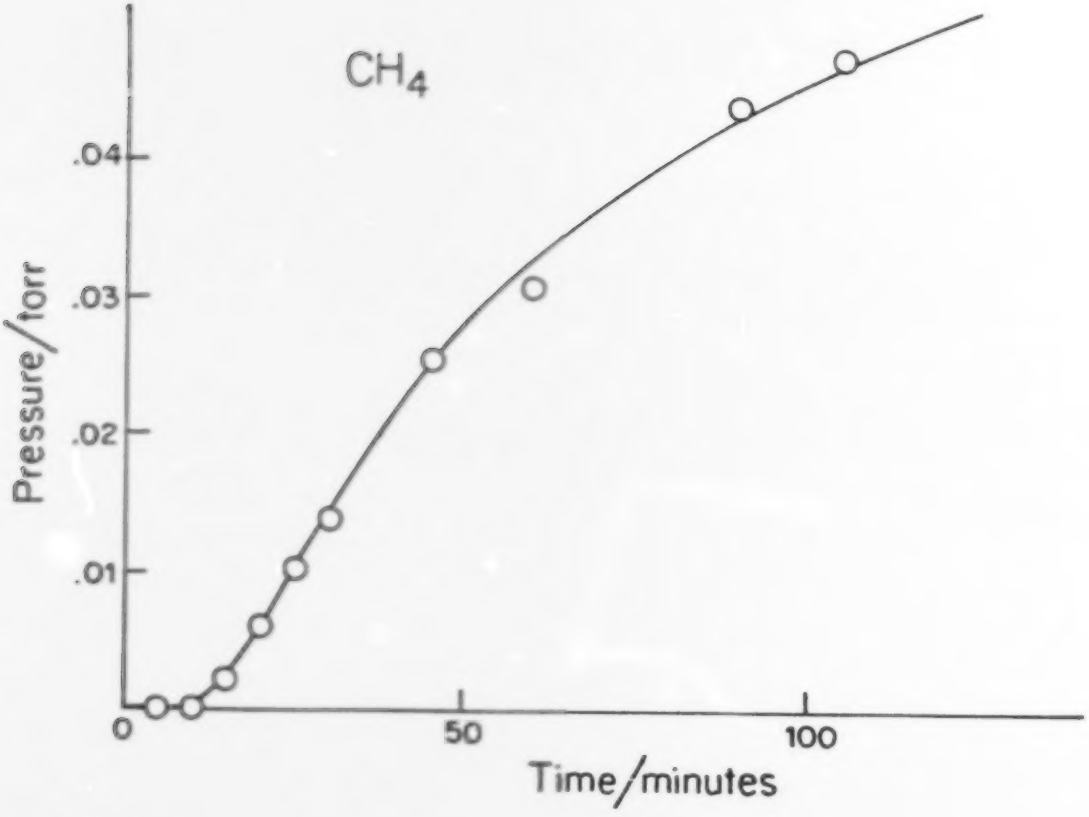

CH_4
.04
.03
.02
.01
Pressure/torr
0
50
100
Time/minutes

FIGURE 8